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A custom absorption trap capable of concentrating the VCM from one liter (or more) of ambient air was used to extend the lower detection limit. Using a custom trap heating circuit, the concentrated sample can be thermally eluted into the GC in a gas volume of 10 ml or less, providing a 100-fold increase in sensitivity compared to that obtained with a 10 ml sample loop.

Preliminary system and final acceptance test results are reported in detail. These test results indicate that a monitor of this type can detect less than one part per billion (ppb) of VCM in ambient air operating on a 15-minute cycle. If the concentration trap is replaced by a 20 ml sample loop, the limit of detection is estimated to be about 35 ppb VCM when operating on a 5-minute cycle.

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ABSTRACT

A monitor for vinyl chloride monomer (VCM) in ambient air was constructed using commercially available components of a gas chromatograph (GC) coupled with a chemiluminescence ozone analyzer slightly modified to make it suitable for use as a GC detector. The specificity for VCM is enhanced by use of a chemiluminescence detector because saturated hydrocarbons do not chemiluminesce with ozone. A custom GC oven and monitor cabinet were used to make it possible to transport the monitor in a standard station wagon for purposes of field evaluation.

A custom absorbtion trap capable of concentrating the VCM from one liter (or more) of ambient air was used to extend the lower detection limit. Using a custom trap heating circuit, the concentrated sample can be thermally eluted into the GC in a gas volume of 10 ml or less, providing a 100-fold increase in sensitivity compared to that obtained with a 10 ml sample loop.

The results of testing at the component level are reported in detail. These results imply that the ultimate sensitivity of the technique may be set by the stability of the ozone concentration delivered to the chemiluminescence detector. Specifically, ozone appears to decompose with photon emission at a rate of about four percent per hour.

Preliminary system and final acceptance test results are also reported in detail. These test results indicate that a monitor of this type can detect less than one part per billion (ppb) of VCM in ambient air operating on a fifteen-minute cycle. If the concentration trap is replaced by a 20 ml sample loop, the limit of detection is estimated to be about 35 ppb VCM when operating on a five-minute cycle.

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1.0 INTRODUCTION

1.1 PURPOSE OF CONTRACT

The basic purpose of this contract was to combine existing instrumentation and known techniques to produce a vinyl chloride monomer (VCM) monitor of very high sensitivity and specificity, packaged in a form suitable for transport in a standard station wagon to facilitate field evaluation of the monitor for the measurement of VCM in ambient air. EPA personnel had previously demonstrated the basic sensitivity and specificity for VCM of a gas chromatographic separation technique combined with a chemiluminescence detector. Absorption of VCM on a charcoal bed as a means of sample collection and concentration had also been previously demonstrated.

1.2 SCOPE OF CONTRACT

The contract required interfacing and packaging commercially available process gas chromatograph (PGC) components with a commercially available chemiluminescence analyzer as the detector. The sensitivity of this analysis approach was to be extended by using a "trap" to extract VCM (and other hydrocarbons) from a relatively large volume of air sample. A previously developed trap with a temperature control capable of causing a very rapid thermal step change for rapid elution of the collected sample was selected. With this trap the detection limit was extended to five parts per billion (ppb) of VCM, with an analysis cycle time of less than 30 minutes. Off-the-shelf equipment was used to the maximum extent permitted by size constraints. Special components were fabricated with minimal documentation to ensure that the bulk of the funds expended would be available for initial tests, optimization, and further testing.

1.3 GENERAL APPROACH AND BACKGROUND INFORMATION

Gas chromatograph (GC) techniques are well known and require no detailed description here. A Beckman Instruments, Inc., Model 6700 Process Gas Chromatograph Programmer was used to provide the basic programmable timing and control functions. Two standard Beckman PGC 10-port valves were used for valving a sample trap, a stripper column, and an analysis column into various independent and/or series gas flow circuits upon commands from the programmer. The stripper and an analysis column were designed and fabricated by the Applications Engineering Department of the Process Instruments Division of Beckman Instruments, Inc. In final acceptance testing, an analysis column previously tested by the EPA was substituted for the Beckman analysis column.

A Beckman Model 950 Ozone Analyzer (chemiluminescence type) was modified for monitoring vinyl chloride. The major modifications were:

- Addition of a standard Beckman ozonator, consisting of a quartz envelope mercury vapor lamp, properly housed, and a ballast transformer power supply.

- Modification of the internal plumbing to provide for selection of either air (supplied by a built-in pump) or oxygen flow through the ozonator, and to permit use of one of the two built-in flowmeters for monitoring the ozonator supply flow rate, and use of the other flowmeter for monitoring the total flow being discharged from the chemiluminescence reaction chamber.

- The addition of an absorber to remove trace contaminants from the ozonator supply, and of an ozone absorber in the gas effluent line to prevent the discharge of ozone to the atmosphere.

- Rewiring of the Model 950 power switch to make it control the ozonator power supply only.

- Modification of the Model 950 reaction chamber to make it about three times the standard depth, which increased the sensitivity to vinyl chloride about three-fold.

In the modified instrument the carrier gas effluent from the GC section is blended with an ozone-rich air (oxygen) stream in the Model 950 reaction chamber. VCM, as well as other components which chemiluminesce when they react with ozone, is detected quantitatively by a photomultiplier tube positioned adjacent to the reaction chamber.

The major advantage of a chemiluminescence detector for this application lies in the fact that saturated hydrocarbons, which might not be satisfactorily separated by the GC portion of the monitor, do not produce a chemiluminescence signal. The specificity of the monitor is, therefore, greatly improved by the use of this detector instead of one of the ordinary GC detectors of comparable sensitivity, such as the flame ionization detector, which responds to all hydrocarbons.

A custom GC oven was purchased in order to meet the contractual size constraints for the monitor. The GC valves and columns were mounted within the custom oven. A hot-air-bath-type temperature control was employed. A standard Beckman circuit board (with minimal modification) was used to control the oven temperature.

The VCM trap and trap thermal control circuitry were adapted from a previous contract performed for the EPA by Beckman (Contract No. 68-02-0778). Hand-wired breadboard circuitry was employed, as on the prior contract, to avoid unnecessary cost for an evaluation prototype.

All custom components were mounted in one compartment of the monitor console, which is referred to as the control module in this report. These included:

- The trap and the trap temperature control circuit board.
- The GC oven and its temperature control circuitry.
- All gas pressure gages, flow control valves, and flow indicators (except flow indicators and controls included in the Model 950 chemiluminescence monitor).
- Power distribution terminal blocks and fuses for each component of the monitor.

The trap can be easily removed and replaced by an ordinary GC "sample loop" if desired. The maximum volume of the sample loop is determined by the ability of the GC columns to handle such hydrocarbons as ethylene and propylene, which normally elute before VCM. If the concentrations of these hydrocarbons are too high and the sample loop volume is too large (approaching 20 mℓ), the columns are saturated by the other constituents and the VCM peak is obscured by tailing of the prior peaks. However, since the trap employed has a lower capacity for ethylene and propylene, these hydrocarbons may saturate the trap and break through during the trap loading cycle without affecting the trap retention of the VCM. When the trap is valved into series flow with the GC columns and heated to elute the hydrocarbons, the limited ethylene and propylene capacity of the trap prevents overloading of the column (up to much higher concentrations). The relatively high VCM capacity of the trap permits concentration of the VCM from more than one liter of sample. The net effect permits concentration of the VCM by a factor of at least 50 without producing overlapping peaks due to comparable concentrations of ethylene, propylene, etc. which occur when larger volume sample loops are employed.

The use of an ordinary sample loop (5- or 10-mℓ volume) instead of the trap may be beneficial if relatively high (20 ppm or more) VCM concentrations are to be monitored.

2.0 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

2.1 SUMMARY

This essentially hardware-oriented project was conducted to provide a highly specific and sensitive monitor for vinyl chloride monomer (VCM) in ambient air. Standard, commercially available instrumentation was combined with a minimum quantity of custom designs to provide a monitor suitable for transportation in a standard station wagon to facilitate field evaluation.

The monitor developed uses gas chromatographic (GC) equipment and techniques to isolate VCM from related and potentially interferring compounds, and a chemiluminescence analyzer as the GC detector to further increase the specificity of the system. A charcoal (or equivalent) trap is used to concentrate the VCM contained in up to one liter of sample into a volume of a few milliliters suitable for injection (by thermal elution) into the GC carrier gas stream.

The results of tests performed on the major components before integration into the monitor are reported, with emphasis on the theoretical and practical implications of the test results. The tests performed on the monitor prior to delivery to the EPA, and the results obtained, are also reported in detail.

The results of Final Acceptance Testing at the EPA facility are also contained in this report. In the final test configuration the VCM analysis was free from interferences from pollutants in the prevailing ambient air. An analysis cycle of less than 15 minutes would detect less than 2 parts per billion (ppb) of VCM. The long-term stability was such that when operated with a full-scale operating range of 0-100 ppb VCM or more the monitor should not require calibration more often than once per week.

2.2 CONCLUSIONS

It may be concluded from the results of the work performed on this contract that a VCM monitor capable of reliably detecting less than 5 ppb VCM in ambient air with less than a 15-minute operating cycle can be produced. Commercially available major components plus some custom components which are not available off the shelf are required. Monitors of this basic design will fit in a station wagon for convenience in monitoring the ambient air in selected areas for VCM concentration.

Most of the VCM-related compounds which may be expected to be present when VCM is detected do not interfere with the VCM analysis. It is more difficult to discriminate against several unknown atmospheric pollutants and components of cigarette smoke than it is to separate VCM from ethylene, propylene, 1-butene, and the dichloroethylenes.

2.3 RECOMMENDATIONS

It is recommended that the VCM monitor be subjected to additional laboratory interference testing. In particular, identification of those unknown atmospheric pollutants and cigarette smoke components which were eluted from the GC column at very nearly the same time as the VCM would be of value for future field evaluation.

Field testing of the monitor in localities where traces of VCM are expected to exist in the ambient air is of major interest. The results of all tests performed on this contract indicate that the field tests should be highly successful.

Sample collection trap absorbers other than charcoal should be evaluated. In particular, it is known that the trap provided with the monitor has very little capacity for ethylene, which can be of advantage when large concentrations of ethylene are present because overloading of the GC columns is prevented by the small ethylene capacity. However, this is a disadvantage when and if it is desired to monitor ethylene too. Similarly, the propylene peaks are not linear with sampled volume, which might be due to marginal trap capacity, making quantitative analysis for propylene difficult. (Nonlinearity of the chemiluminescence detector itself for propylene has been reported elsewhere, making it difficult to estimate the charcoal trap efficiency for propylene.) Logically, other trap materials will have complementary advantages, broadening the applicability of the technique.

Finally, other applications of the instrumental techniques used in the VCM monitor should be considered. All compounds convertable to NO, H_2S, or mercaptans, for example, can be monitored by this technique. The specificity, sensitivity, and stability of this analysis technique make it very attractive.

3.0 TESTING OF COMPONENTS OF VCM MONITOR

3.1 TRAP TEMPERATURE PROFILE DATA

The details of the trap design are shown in FIGURE 1. A special trap temperature controller, capable of rapidly ramping the trap temperature, was employed in all tests. A test was performed on an empty trap, using a small thermocouple inserted at various distances into the trap to determine the time required to reach 250°C after initiation of the heat cycle. The trap temperature controller was adjusted to provide a steady-state temperature of about 250°C at a central location in the trap. The sequence was: locate thermocouple; apply heat and record temperature *vs* time; turn power off; relocate the thermocouple for the next test as the trap cooled back to ambient temperature. The data, tabulated in TABLE 1, are in units of distance from the end of the trap tube farthest from the temperature controlling thermistor, and in units of time required to reach 250°C after application of power.

While the temperature profile was not completely uniform, subsequent measurement of the elution peak time indicated that elution occurred with a half-bandwidth of about six seconds.

TABLE 1. TEMPERATURE VS TIME PROFILE OF EMPTY TRAP

Thermocouple Location Relative to One End of Trap Tube		Time after Application of Power Required to Reach 250°C	Remarks
(Centimeters)	(Inches)	(Seconds)	
0.64	0.25	12	←Start trap fill at 1 cm
1.27	0.50	24	↑ Position of Coconut Shell Charcoal in Typical Filled Trap
1.91	0.75	36	
2.54	1.00	48	
3.17	1.25	60	
3.81	1.50	60	↓
4.44	1.75	48	←End trap fill at 3.8 cm
(Adjacent thermistor)			

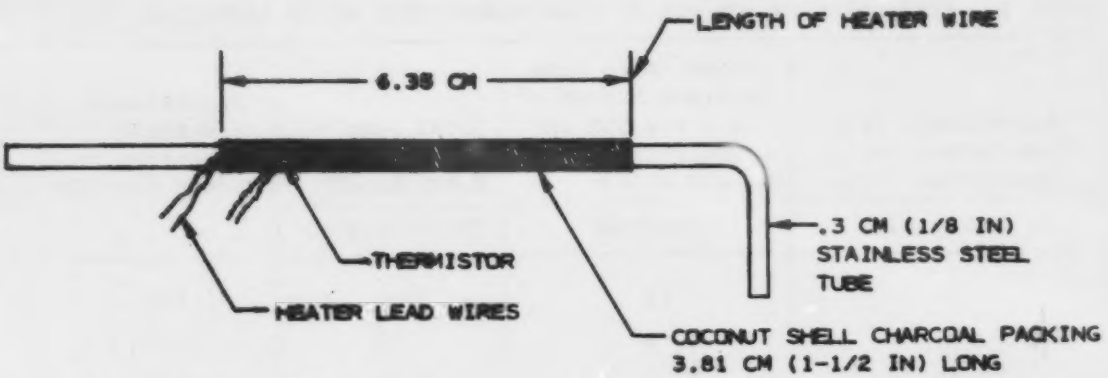


Figure 1. Design of VCM Trap

3.2 TRAP CAPACITY AS A FUNCTION OF AMBIENT TEMPERATURE

A trap charged with coconut shell charcoal was connected in series with the inlet to a flame ionization detector. A gas mixture of 2.6 ppm VCM in nitrogen was passed through the trap at 150 mℓ/min. Between tests at various trap temperatures (simulating various ambient temperatures), the trap was heated and stripped free of hydrocarbons by a flow of nitrogen. After cooling to the new ambient temperature, the trap was reconnected to the 2.6-ppm VCM sample at a flow rate of 150 mℓ/min. The flame ionization analyzer output, which was recorded continuously, served to indicate the time to breakthrough of VCM. The results of these tests are given in TABLE 2.

The trap temperature during the collection was not precisely known because the air-bath oven could not be closed during the test. The tabulated maximum concentration factors for VCM are computed with a 10-mℓ sample loop as a reference. This is a reasonable size since tests indicated that an 18.5-mℓ sample loop gave reasonably satisfactory results, but that a 32-mℓ sample loop made the system performance too dependent on ethylene and propylene concentrations. It may be concluded, therefore, that a concentration factor of at least 50, up to a trap temperature of 55°C during sample collection, can be obtained.

3.3 TRAP ELUTION TEST

A sample gas containing 2.6 ppm VCM in nitrogen was passed through the trap at a flow rate of 150 mℓ/min for six minutes and 45 seconds, giving a total sample of 1.01 liters. The trap was then connected in series with a standard flame ionization detector (FID) with a nitrogen carrier gas flowing. After the FID output stabilized, the trap temperature controller was energized (set for 250°C). The recording of the FID output indicated that the VCM peak reached the FID two seconds after the trap heat was applied. The peak response occurred at 12 seconds, and the response was below 10% of the peak

TABLE 2. TRAP CAPACITY FOR VCM VS TRAP TEMPERATURE WHILE ABSORBING

Approximate Trap Temperature during Absorption Cycle	Approximate Time to Breakthrough of 2.6 ppm VCM in Nitrogen at 150 mℓ/min	Total Sample Volume Before Breakthrough	Approximate Maximum Concentration Factor for VCM
(°Centigrade)	(Minutes)	(Milliliters)	
30	12	1800	180
40	9	1350	135
50	9	1350	135
55	7	1050	105

value in 18 seconds. The VCM peak was reasonably symmetrical, with a half-bandwidth of about six seconds.

3.4 COLUMN ELUTION TIMES FOR SEVERAL COMPONENTS

Stripper and analysis columns were obtained from the Beckman Applications Engineering Department. The stripper column was 1.6 m long, standard stainless-steel, GC grade, 1/8" OD tubing. It consisted of an upstream section 1.3 m long packed with 30% dioctyl adidate on Chromosorb P, 45/60 mesh, and a downstream section 0.3 m long containing Poropak (200-2) Q, 50/80 mesh. The analysis column was a 1.0 m long, standard stainless-steel, GC grade, 1/8" OD tubing containing Poropak (200-2) R, 50/80 mesh.

Two columns of each type were obtained. They were preconditioned by heating to 120°C for one hour with a flow of 40 mℓ/min of nitrogen. They were then controlled at 95°C for subsequent testing.

Each column was tested using the trap (with thermal ramp elution) for sample injection, and the standard FID analyzer as the detector. The results of these tests are given in TABLE 3.

3.5 OZONATOR TESTS

The ozone generator (ozonator) employed is of Beckman design, using a Western Quartz, Inc., mercury vapor, quartz envelope lamp. A stream of air (or oxygen) flows through a Teflon tube surrounding the lamp, and then to the reaction chamber through small-bore Teflon tubing. Part of the oxygen, in passing through the lamp housing, is converted to ozone by action of the ultraviolet (UV) light emitted by the lamp. Tests performed under this contract indicated that the following conditions prevail:

TABLE 3. ELUTION TIMES OF SEVERAL HYDROCARBONS FOR TWO STRIPPER AND TWO ANALYSIS COLUMNS PROVIDED BY THE BECKMAN APPLICATION ENGINEERING DEPARTMENT

Column Identification	Elution Times (at Peak) for Several Hydrocarbons in Minutes after Applying Power to Trap		
	VCM	*1,2-dichloroethylene *cis*	*1,2-dichloroethylene *trans*
Analysis Column--No. 1	1.5	5.5	8.5
No. 2	1.5	-	-
Stripper Column--No. 1	1.4	3.7	5.5
No. 2	1.2	3.2	4.8

*Identification of these compounds was later found to be doubtful. These data are consistent with the vendor tag on the cylinder received, but this was not what was ordered. Several other mixtures were tested later, but it was not possible to prove whether the cylinder tag, the purchase order, or neither was correct.

- The ozone concentration of the effluent gas is independent of gas flow rate up to about 160 mℓ/min, above which the concentration of ozone decreases.
- The maximum achievable ozone concentration is approximately proportional to the square root of the oxygen concentration of the gas used.
- When stored in a glass spectrophotometer cell with rock salt windows, the ozone decomposes at a rate of roughly 4%/hour.

The tests which resulted in these observations were neither repeated nor pursued further. Any conclusions drawn are, therefore, merely speculative pending further investigation. A thorough literature search, which was beyond the scope of this effort, might provide a complete understanding of the ozone formation and decomposition mechanisms. However, the implications of these observations are sufficiently interesting to warrant further mention in this report.

These observed results may be predicted from a simple theory which assumes reasonable mechanisms for the ozone formation and decomposition reactions. In particular, the constancy of ozone concentration with flow rates below about 160 mℓ/min suggests that a steady state (equality of formation and decomposition rates) is being attained in less time than the gas spends in the

ozonator. The rate of formation of ozone will be proportional to the incident ionizing radiant energy density and to the concentration of oxygen if the rate-governing step involves interaction of photons with isolated oxygen molecules. The rate of decomposition will be proportional to the square of the ozone concentration if decomposition involves the simultaneous collision of two ozone molecules (either in space or at a wall). Under steady-state conditions the two rates must be equal and, if these assumed mechanisms are correct, it follows that the concentration of ozone will be proportional to the square roots of the oxygen concentration and of the ionizing radiant energy density. A single test (discussed further below) of the effect of lamp current on concentration indicated roughly a 40% increase in ozone for a factor of two increase in lamp current, which is not conclusive, but is supportive evidence.

No evidence regarding decomposition of ozone by molecular collisions at the walls was found. This is a possible, but considered improbable, reaction mechanism. If a simultaneous collision of two ozone molecules with the wall is involved, a higher concentration of ozone should result if the inside diameter of the Beckman ozonator is increased, since this would increase volume more rapidly than surface area. Increasing the length of the ozonator should have no effect, since the volume and surface both increase linearly with the length of a cylinder. If collisions of two ozone molecules in space are involved in the decomposition reaction, then altering the reaction chamber dimensions will have no effect on the maximum ozone concentration. The slow rate of decomposition of ozone in a glass cell, discussed further below, suggests that neither the walls nor merely the simultaneous collision of two ozone molecules is involved in the rapid decomposition rate occurring within the ozonator. Another factor is probably involved, as explained below.

In order to account for a rapid rate of decomposition in the ozonator compared to that outside the ozonator (discussed further below), it is sufficient to assume that the rate of decomposition is proportional to the square of the ozone concentration and to the lamp intensity. It would then be necessary that the ozone formation rate be proportional to P_{O_2} and to the square of the lamp intensity in order to account for the observed proportionality between equilibrium ozone concentration and the square root of both P_{O_2} and the lamp current.

Measurements of the IR absorbance at 1020 and 1052 cm^{-1} wave numbers indicate that up to about 1% ozone can be obtained from the Beckman ozonator when using oxygen and the larger of two ballast transformers. This estimate is based on published values for the specific absorbance of ozone at these wave numbers. Absorbance in the UV region was not measured because a suitable spectrophotometer was not available at the time. A measurement of the apparent ozone concentration due to the decrease in paramagnetic susceptibility of air passed through the ozonator indicated that about 0.32% ozone (maximum) was obtained using air (up to 80 mℓ/min or more) and a smaller ballast transformer, which fixed the lamp current at about one-half that of the larger transformer used to obtain about 1% ozone with oxygen. Using the square root of both the lamp current and of the oxygen concentration to calculate the ozone concentration to be expected from the larger ballast transformer, and for 100% oxygen instead

of air, one obtains 0.32% ozone $\sqrt{(2)(100/21)}$ = 0.99% ozone, which is an amount in good agreement with the spectroscopic data noted above. Using oxygen and the smaller ballast transformer (which is used in the monitor), one would expect about 0.7% ozone maximum. A similar test, using several similar ozonators, was made subsequently at Beckman on a different project. These IR absorption tests indicated that about 0.7% ozone was the maximum attainable, rather than 1%, with the larger transformer. In the configuration delivered it may be concluded that between 0.5 and 0.7% ozone can be obtained using an oxygen supply, and that between 0.2 and 0.3% ozone can be obtained using air.

The spontaneous decomposition rate of ozone was roughly determined by noting that the IR absorbance decreased to about 1/3 of the initial value in 17 hours, indicating a decomposition rate of about 4% of the ozone per hour when stored in a glass cell with rock salt windows. It is also possible to obtain an estimate of the spontaneous ozone decomposition rate in the reaction cell of the Model 950. The zero offset of the Model 950 with about 0.7% ozone, but with no VCM or other known reactant present, is known. This output is equivalent to that which would be observed if a sample containing about 0.05 ppm ozone were to be blended with an excess of ethylene in the reaction cell at a flow rate of 13.3 mℓ/s (which is the normal operating mode of the Model 950 as an ozone monitor). It is known that 50 to 100% of the ozone reacts in the cell under these conditions and that the sample residence time in the cell is about one second. It may be inferred that an equivalent amount of ozone spontaneously decomposes in the cell each second when 0.7% ozone is present. It is necessary to assume that the spontaneous decomposition of ozone also results in photon emission. It is then possible to estimate the spontaneous decomposition rate to be about $(0.5 \times 10^{-6})/(7 \times 10^{-3})$ per second. This corresponds to 7×10^{-4}% per second, or 2.6% per hour. This agrees (within about a factor of two) with the spontaneous decomposition rate observed in the IR absorption cell, discussed above.

One implication of these data is that the observed zero offset of the VCM monitor is due to an ozone decomposition reaction accompanied by chemiluminesence. This reaction must be slow compared to the decomposition rate which occurs within the Beckman ozonator. Further implications are that the decomposition reaction outside the ozonator is probably first order rather than second order with the ozone concentration, and that the high rate of decomposition of ozone in the ozonator is due, therefore, to the interaction of two ozone molecules with a UV photon, rather than to merely the collision of two ozone molecules. The UV photons causing decomposition would have a flux density proportional to that of those causing ozone formation for given lamp operating conditions. The spectral energy distribution of a lamp of this type would be expected to remain constant over a fairly wide range of lamp current, for which the lamp voltage drop is constant. Over this current range the energy output is, therefore, linear with lamp current. While it is probably the case, it was not shown that the Beckman ozonator lamp operates in this current range for both transformers tested (30 and 60 mA nominal currents).

3.6 REACTION CHAMBER DESIGN

The standard reaction chamber of the Beckman Models 950, 951, and 952 chemiluminescence analyzers is only approximately 2.5 mm (0.1 inch) deep. This is an adequate depth for the standard analyzers, but it did not appear to be adequate for the vinyl chloride/ozone reaction. It was found that the same net signal was obtained for flow rates of about 16 to 160 mℓ/min each of ozonated air and 2.6 ppm vinyl chloride in nitrogen. The technique of making corresponding changes to retain a constant ratio of the two flow rates provides fixed ozone and VCM concentrations. The gases were passed directly into the Model 950 reaction chamber in this series of experiments. The 2.6-ppm VCM in nitrogen sample was replaced by nitrogen for each flow setting to provide a zero VCM signal. The major observations resulting from these experiments were:

- The sensitivity to vinyl chloride is dependent on the product of the concentrations of vinyl chloride and ozone only.
- The maximum signal occurs when the flow rates of sample and ozonated air are equal, which maximizes the product of VCM and ozone concentrations.
- The zero offset is essentially constant for equal flow rates of VCM and ozone-rich gas from 16 to 160 mℓ/min, indicating that the offset is dependent on the ozone concentration only. (Note that the ozone concentration in the stream from the ozonator was constant for flow rates below about 160 mℓ/min.
- The above results indicate that only a small percentage of the vinyl chloride reacts in the chamber, probably less than 10% even at the low flow rate of 16 mℓ/min of each gas.

The chamber depth was subsequently increased by about a factor of three to increase the percentage of VCM which reacted in the chamber.

4.0 SYSTEM TESTING

4.1 LINEARITY OF PEAK HEIGHT WITH SAMPLED VOLUME

The Model 6700 Process Gas Chromatograph (PGC) Programmer provides for convenient selection of sample collection time. A measure of the efficiency of the trap for VCM collection is provided by maintaining a fixed sample flow rate while varying the time of collection. A plot of VCM peak height *versus* sample collection time should be a straight line passing through the origin, provided the flow rate and collection times employed are within the range of 100% trap efficiency. A test was performed using a 200 mℓ/min flow rate (room conditions) of nitrogen containing 1 ppm each of ethylene; propylene; 1-butene; VCM; 1,1-dichloroethylene; and *trans* 1,2-dichloroethylene. The sample was collected in the trap for 0.5, 1, 2, 3, 4, and 5 minutes. The chromatogram for a two-minute collection time using a recorder chart speed of one inch per minute is shown in FIGURE 2. FIGURES 3, 4, and 5 are chromatograms for the 0.5-, 1-, 2-, 3-, 4-, and 5-minute collection times, using a chart speed of 0.1 inch per minute. The operating conditions are fully described on FIGURE 2 for convenience of reference. The data on the other figures stress the deliberate changes made in operating conditions.

It should be noted that peak number 5 of these figures is believed to be an impurity in the sample, and that (a) either one of the two dichloroethylenes does not chemiluminesce, or (b) they elute together, or (c) the wrong material was employed in making the sample. Manual injection of additional 1-butene during the trap-loading cycle caused an increase in peak number 4 without altering peak number 5 significantly. Similar tests indicated that peak 5 was not due to the dichloroethylenes, and that the two dichloroethylenes were possibly eluting simultaneously, but data from two other mixtures merely increased the confusion. One mixture called for 1,1- and 1,2-dichloroethylene on the purchase order, but its label indicated that *cis* and *trans* 1,2-dichloroethylene were used. This mixture gave two distinct peaks during component testing when using the FID, but only one peak in the system tests with the chemiluminescence detector. It is probable that one of the samples in that case was a dichloroethane, which does not chemiluminesce. It is quite possible that a similar error occurred with the other mixtures. It is concluded that the results for the dichloroethylenes were essentially inconclusive.

The peak heights for 1 ppm of VCM, taken from FIGURES 3, 4, and 5, are plotted as a function of collection time in FIGURE 6. It is apparent that zero peak height corresponds to a very small collection time (about 0.1 min), rather than zero time. This was caused by the particular valving and interconnection arrangement employed. Specifically, at the end of a sample collection cycle a solenoid valve positioned upstream of the trap closes and remains closed until

OPERATING CONDITIONS

RECORDER:	CHART SPEED OF ONE INCH/MIN (NOTE THAT 3 MINUTES WERE REMOVED)
	100 mV FULL-SCALE SENSITIVITY
MODEL 950 SETTINGS:	2.5 PPM RANGE AND 0.1-VOLT OUTPUT
	ZERO POT AT 7.00 TURNS
	SPAN POT AT 7.00 TURNS
	RESPONSE SWITCH IN "FAST" POSITION
GC OVEN TEMPERATURE:	90°C
FLOW RATES:	SAMPLE AT 200 ml/MIN, COLLECTED FOR TWO MINUTES
	CARRIER FLOW RATE AT 75 ml/MIN (ROOM CONDITIONS)
	OZONATOR FLOW RATE AT 200 ml/MIN (ROOM CONDITIONS)
SAMPLE COMPOSITION:	NITROGEN, CONTAINING ONE PPM EACH OF THE FOLLOWING (PEAKS ARE IDENTIFIED WHERE POSSIBLE BY CORRESPONDING NUMBERS)
	(1) ETHYLENE
	(2) PROPYLENE
	(3) 1-BUTENE
	(4) VINYLCHLORIDE MONOMER
	(5) UNIDENTIFIED--PROBABLY IMPURITY
	(6) 1,1-DICHLOROETHYLENE AND/OR *trans* 1,2-DICHLOROETHYLENE, EACH PRESENT AT 1 PPM CONCENTRATION

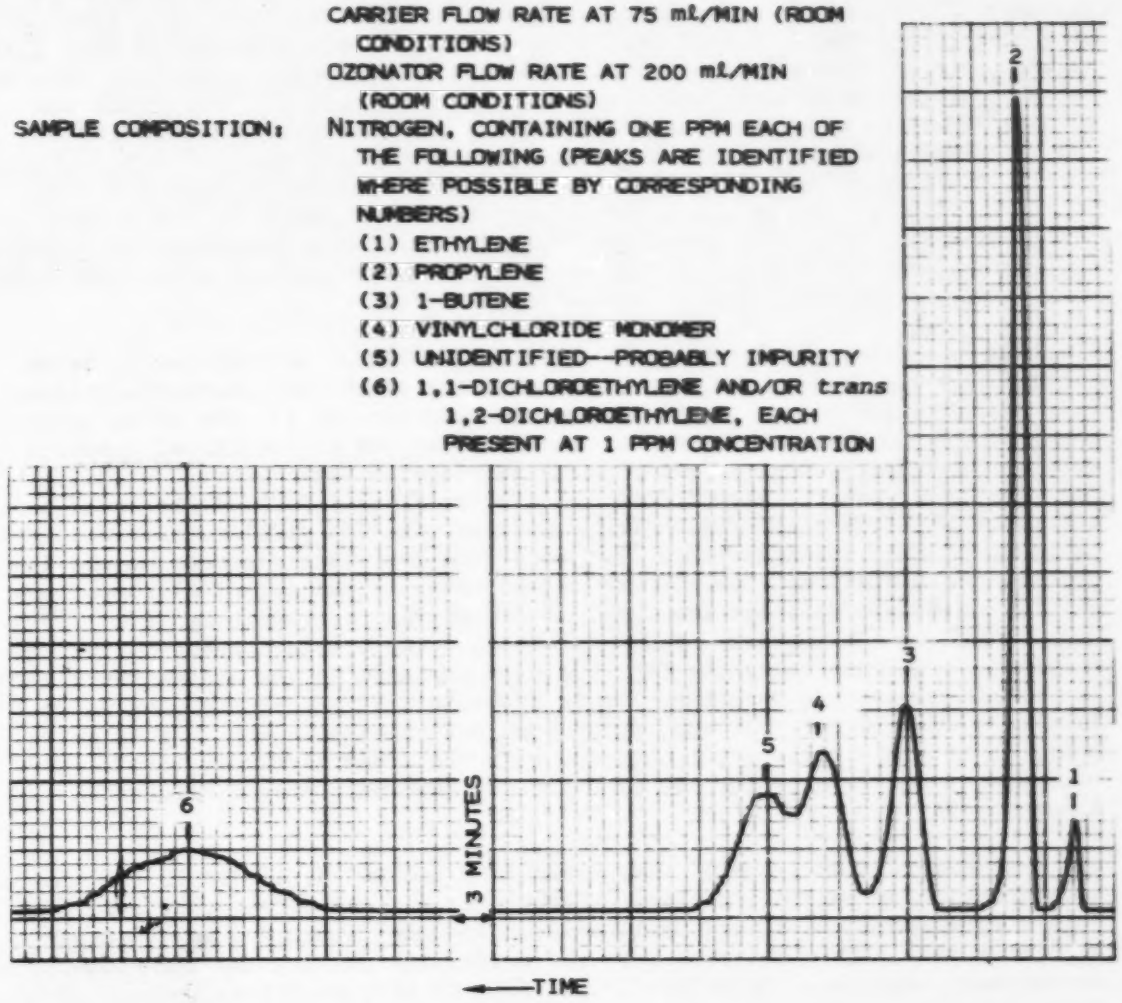


Figure 2. Chromatograms of Six-Component Mixture in Nitrogen, Identifying Peaks where Possible

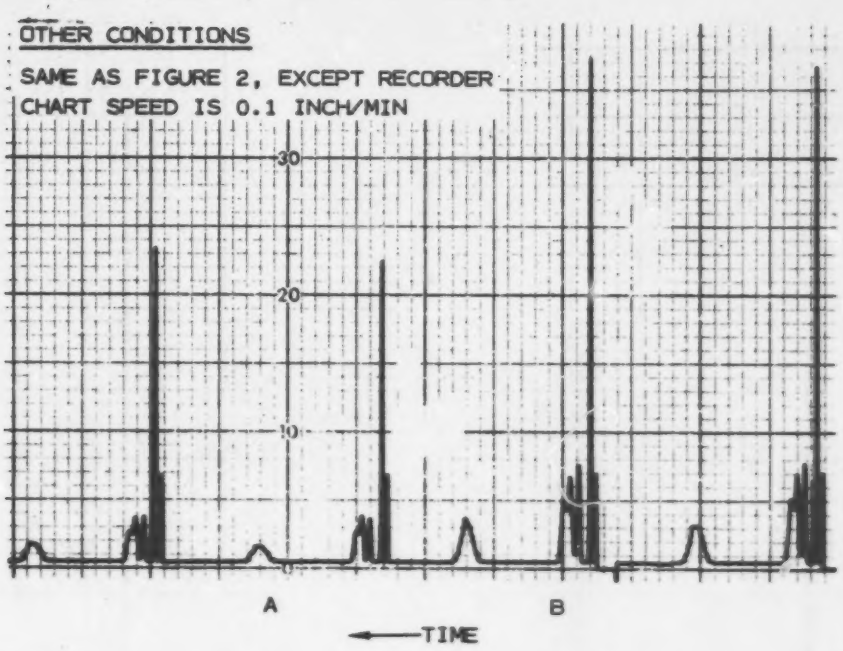
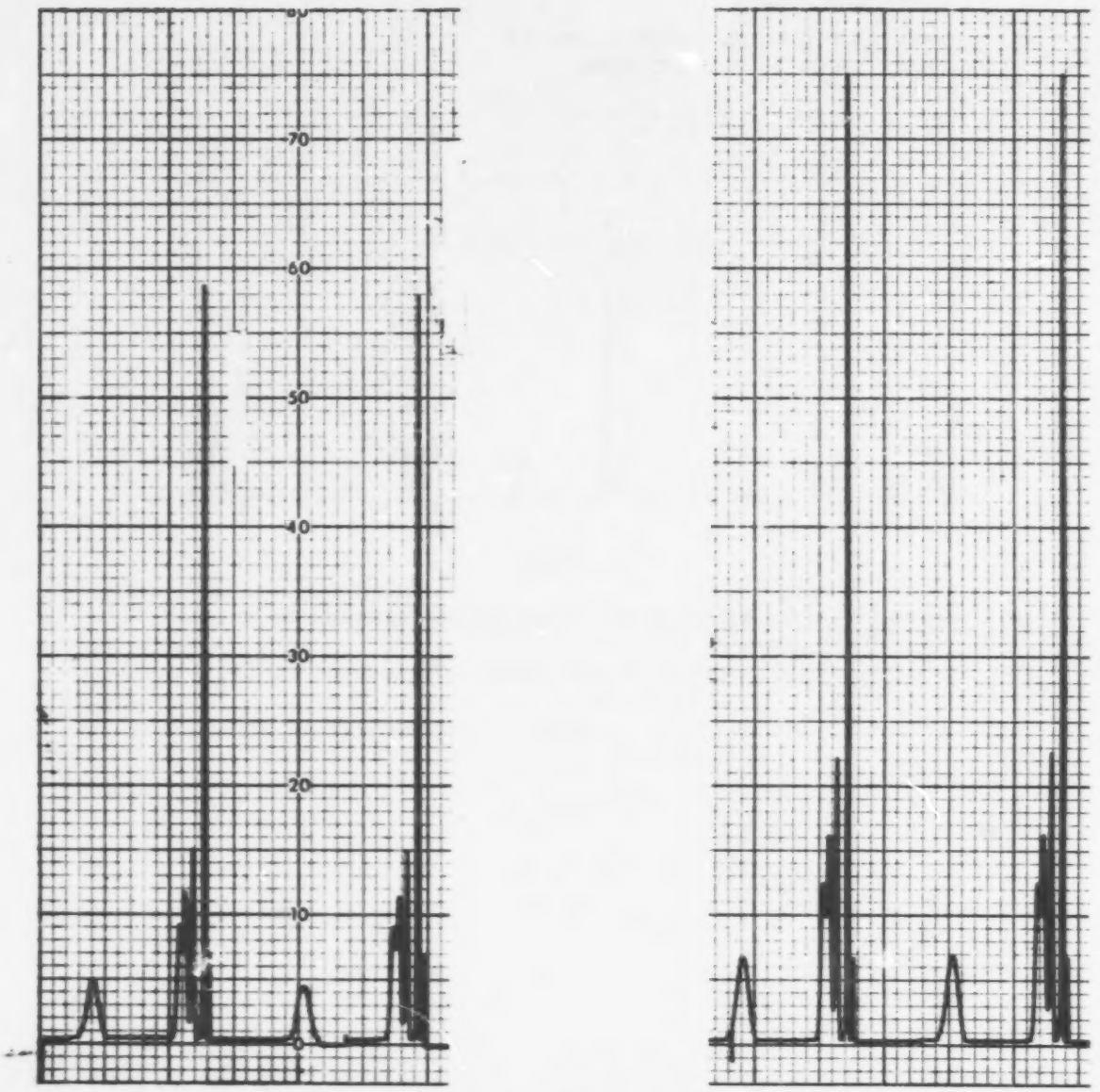


Figure 3. Chromatogram of Six-Component Mixture in Nitrogen for
(A) One-half-Minute Sample Collection Period at 200 mℓ/min
(B) One-Minute Sample Collection Period at 200 mℓ/min



OTHER CONDITIONS

SAME AS FOR FIGURES 3 AND 5

Figure 4. Chromatogram of Six-Component Mixture in Nitrogen for (A) Two-Minute Sample Collection Time Period at 200 mℓ/min, and (B) Three-Minute Sample Collection Time Period at 200 mℓ/min

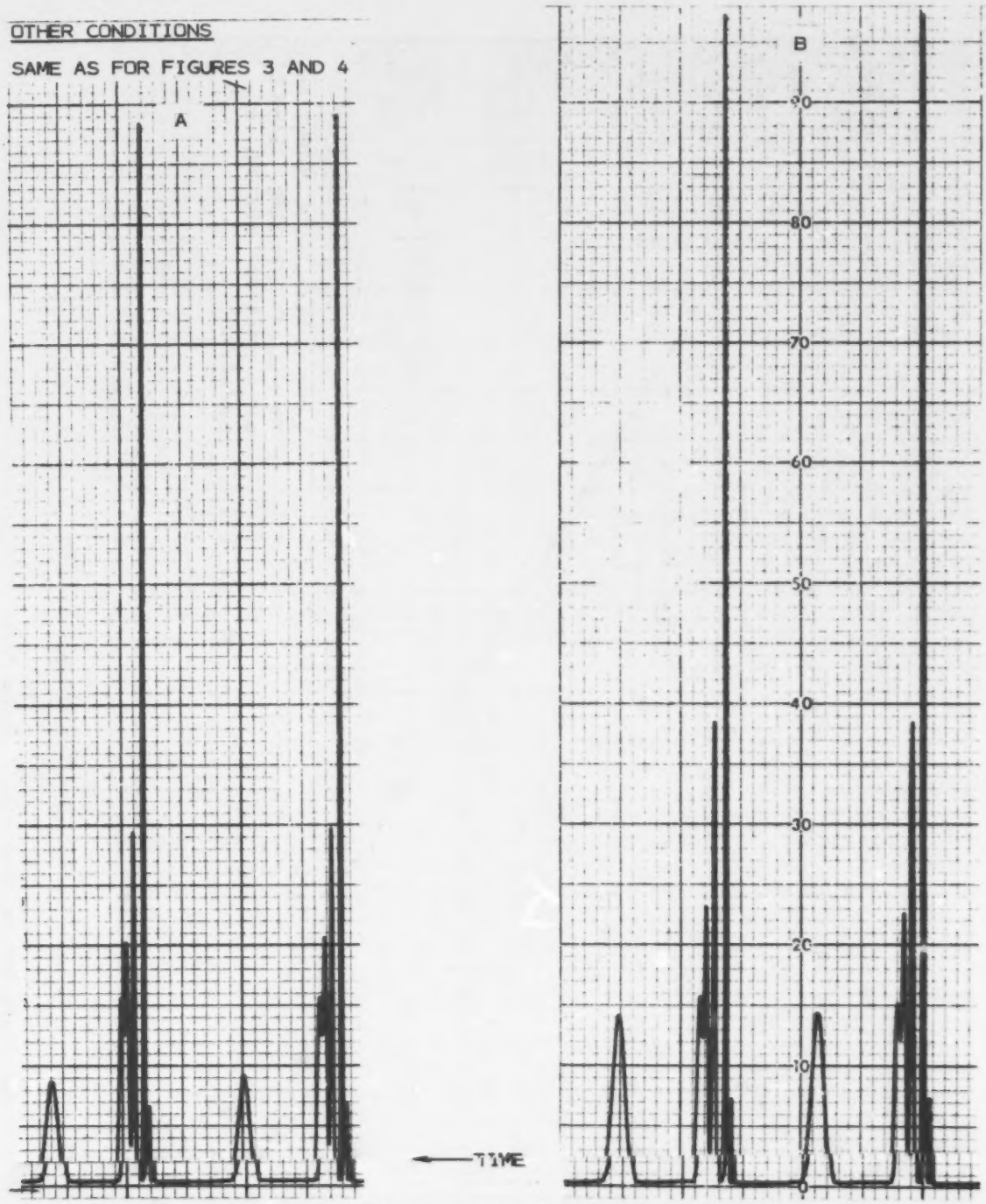


Figure 5. Chromatograms of Six-Component Mixture in Nitrogen for (A) Four-Minute Sample Collection Period at 200 mℓ/min, and (B) Five-Minute Sample Collection Period at 200 mℓ/min

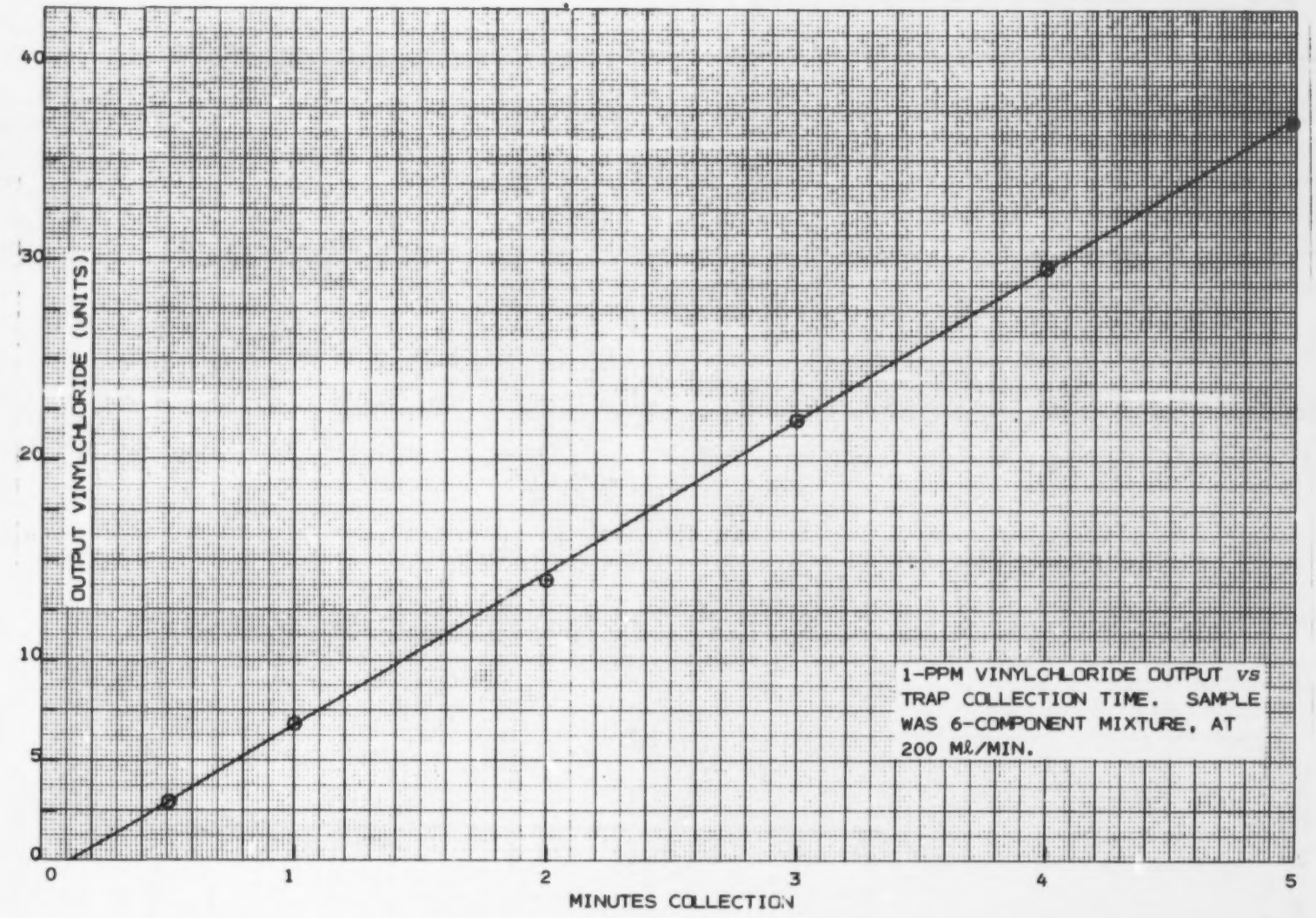


Figure 6. Output for 1-ppm VCM vs Sample Collection Time

the beginning of the next collection cycle. The sample pump is connected to draw sample through the trap, and operates at all times. Thus, the pump evacuates the trap and interconnecting lines during the period of solenoid valve closure. When the valve opens at the beginning of each sample collection cycle, the sample rushes into the trap and interconnecting lines with almost no flow resistance (up to the pump exhaust valve). The net effect is that a volume of sample equal to that of the system between the solenoid valve and the sample pump exhaust valve is added to the calculated volume collected (calculated as flow rate multiplied by time for each collection time). From the data presented, this volume is about 15 mℓ, which is a reasonable value. This defect was not corrected because it was not considered significant for purposes of this contract. However, proper use of a three-way solenoid valve to eliminate this effect would be appropriate for any further development effort.

FIGURE 7 is a plot of all peak heights from FIGURES 3, 4, and 5. The plot for peak number 1, ethylene, clearly indicates that the trap has very little capacity for ethylene. The plot for peak 5 (unknown impurity) indicates that the trap reaches capacity for this component at about four minutes, corresponding to 800 mℓ at room temperature and pressure (RTP). Peak 2, propylene, is nonlinear with sample volume, but complete saturation of the trap is not indicated for up to one liter of sample. The peak height curve for peak number 6 (probably dichloroethylene of one or more types) is not a smooth curve. In retrospect, it is quite possible that a part of this peak was being lost by initiating stripper column back flush prematurely. This would make the peak height very dependent on minor changes in carrier gas flow rate, GC column temperature, etc.

A subsequent test with helium carrier at a 50% higher flow rate yielded a 52% higher value for peak 6, without affecting the other peaks proportionately. This suggests that back flush of the stripper was being initiated too soon when the data of FIGURES 2 through 7 were obtained. The helium carrier test results are discussed further below.

4.1.1 Comparison of Nitrogen and Helium as Carrier Gas

After obtaining the data presented in FIGURES 2 through 7, a new reference chromatogram using nitrogen as carrier was obtained. The major change was that the oven temperature indicated 98°C instead of 90°C at the time of this test. No reason for this change could be determined, but it is probable that the oven cover was not properly closed during this test. Immediately following this test the nitrogen carrier was replaced with helium and a second chromatogram was obtained. A later calibration check of the carrier flowmeter with helium indicated that the helium flow rate was 120 mℓ/min, compared to the nitrogen rate of 75 mℓ/min. No other conditions were different. The two comparative chromatograms are shown in FIGURE 8.

No large improvement in performance was obtained by using helium instead of nitrogen, but the inadvertent use of a higher helium flow rate clouds the results somewhat. There was a 30% increase in VCM and 1-butene peak heights,

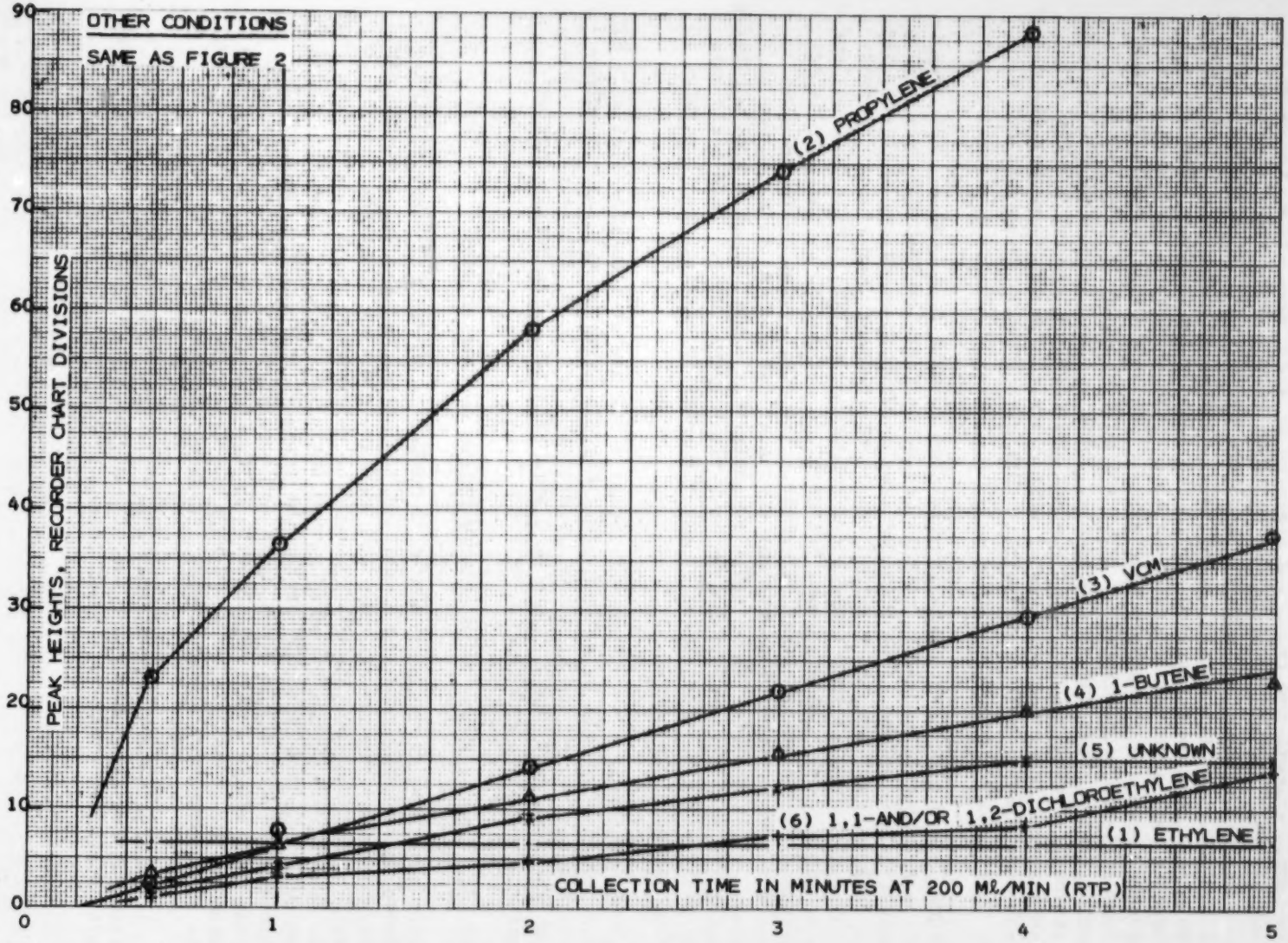
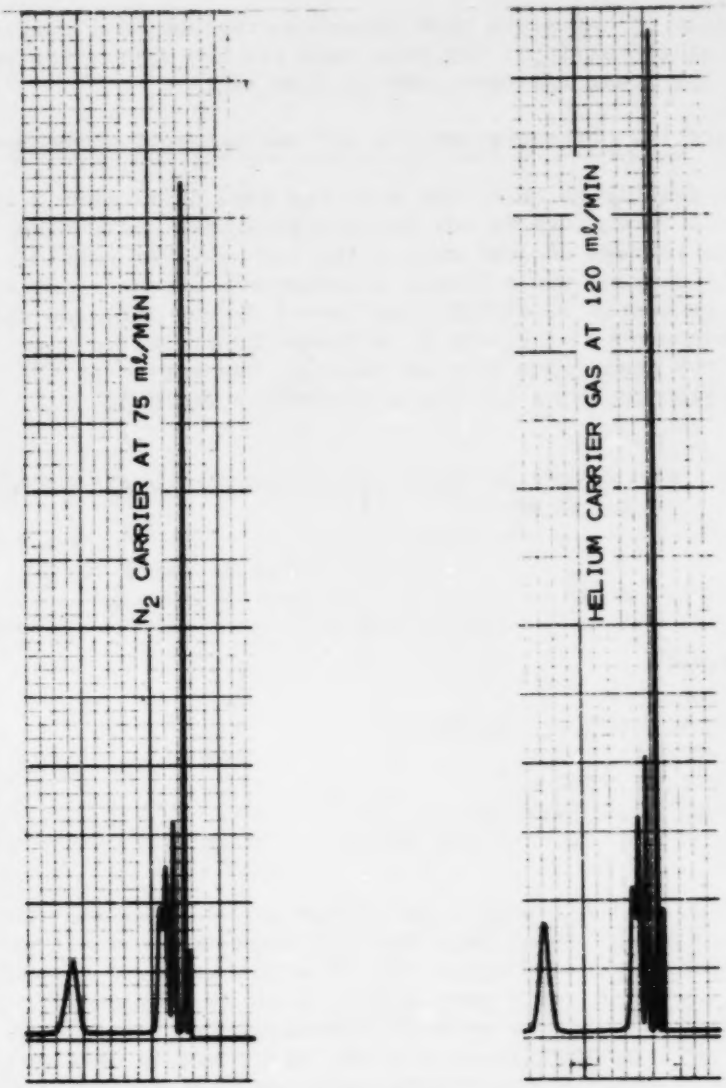


Figure 7. Linearity of all Peak Heights vs Sample Collection Time



OTHER CONDITIONS

SAME AS FOR FIGURES 3 AND 5, EXCEPT AS FOLLOWS:

SAMPLE COLLECTION PERIOD: TWO MINUTES AT 200 mℓ/MIN
OZONATOR FLOW AT 105 mℓ/MIN (FROM 100 mℓ/MIN)
GC OVEN TEMPERATURE: 98°C (FROM 90°C)

Figure 8. Comparison of VCM Monitor Chromatograms when Using Nitrogen and Helium as the Carrier Gas

and a 54% increase in the sixth peak (dichloroethylene(s)), suggesting that the back flush of the stripper may have been set too early, losing part of the sixth peak for the lower nitrogen carrier flow rate.

4.1.2 Comparative Chromatograms for Air and Oxygen for the Ozonator Supply

With conditions exactly as they were when the data of FIGURES 2 through 5 were obtained, several chromatograms for two-minute sample collections were obtained using air instead of 100% oxygen for the ozonator supply. The air was then replaced by oxygen, and a directly comparable chromatogram was obtained. These data are presented in FIGURE 9 as curves A (for air) and curve B (for oxygen). Chromatogram B of FIGURE 9 is almost identical to A of FIGURE 4, verifying that all conditions were as before. The ratios of the peak heights obtained for oxygen to those for air are given in TABLE 4.

TABLE 4. THE EFFECT OF USING OXYGEN INSTEAD OF AIR AS THE OZONATOR SUPPLY

Peak	Ratio of Peaks Using Oxygen to Those Using Air
(1) Ethylene	2.7
(2) Propylene	2.2
(2) Vinyl Chloride Monomer	3.3
(4) 1-Butene	1.9
(5) Unknown Impurity	1
(6) Dichloroethylene(s)	5

From consideration of the reaction mechanisms it would be expected that substances which react with ozone very rapidly, such as NO, would provide outputs which were independent of the ozone concentration (above a minimum excess of ozone). Materials which react more slowly, such as ethylene, propylene, and VCM, would be expected to have outputs approximately proportional to the ozone concentration. In component level testing, discussed in Section 3, results indicated that the ozone concentration would increase approximately as the square root of the oxygen concentration in the supply. It would be expected, therefore, that the ozone concentration ratio was about 2.2 in these tests. The data of TABLE 4 indicate qualitatively that ethylene, propylene, VCM, and 1-butene have slow reaction rates, while the unknown impurity reacts much more rapidly. The unknown was not NO, based on a direct test, but may have been H_2S or a mercaptan. The large increase in the sixth peak sensitivity suggests that a more complicated reaction is involved. The factor of five increase observed would be expected if simultaneous collisions of two ozone and one reactant molecule are required for the chemiluminescence reaction. Similarly, if the reaction involves oxygen as well as ozone then peak ratios larger than 2.2 would be expected.

OTHER CONDITIONS

SAME AS FOR FIGURE 4, CHROMATOGRAM A

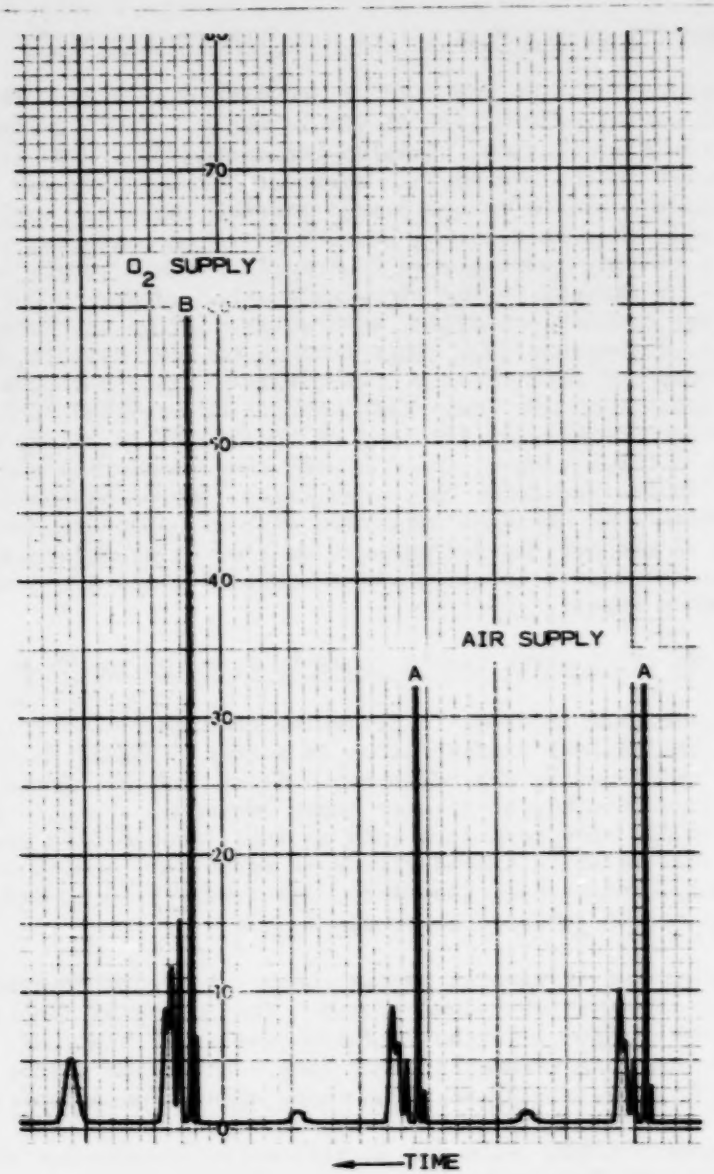


Figure 9. Comparison of Chromatograms Obtained when Using Air instead of Oxygen for the Oxonator Supply

It was beyond the scope of this contract to pursue such questions of reaction mechanisms further. It should be noted that most of the tests reported here were not repeated, and that no firm conclusions should be drawn based on these results.

4.2 LINEARITY OF VCM PEAK HEIGHT WITH VCM CONCENTRATION

The trap concentration time was held at one minute at a flow rate of 150 mℓ/min to provide useful sensitivity to VCM in the 0.5- to 5.0-ppm range, while permitting a rapid cycle time. Samples containing 0.5, 5.0, 1.0, and 2.6 ppm VCM were measured in the system. An apparent nonlinearity was traced to the error in calculated sample volume passed through the trap, explained above. (It was initially thought that the carrier nitrogen contained vinyl chloride, but additional testing demonstrated that no detectable levels of unsaturated hydrocarbons were present in the nitrogen carrier supply.) The agreement between the four available samples, when corrected for the constant volume sampling error, was within ±5%. This fact is noteworthy because the four samples were obtained from three sources, which supports recent US NBS reports that samples containing low concentrations of VCM are stable. Furthermore, this test provided direct confirmation of the linearity of the monitor to VCM in the 0.5- to 5.0-ppm range. Coupled with the demonstration of linearity *versus* sample collection time, discussed above, these results indicated that low VCM concentrations could be monitored with excellent results. Direct demonstration of the monitor performance on lower concentrations of VCM was left for final acceptance testing, the results of which are discussed in Section 5 of this report.

4.3 SYSTEM TESTS USING SAMPLE LOOPS IN PLACE OF THE TRAP

It was of considerable interest to determine the limit of sensitivity which could be achieved without concentration in a trap. Significant preliminary work had been performed by EPA personnel. Using a 25-mℓ sample loop and a chemiluminescence detector of greater depth (which is a better design than the Beckman chamber for slow reactants such as VCM), it had been possible to detect 50 ppb VCM in air. A good figure of merit for the VCM monitor developed on this contract was, therefore, its sensitivity to VCM independent of the ability to concentrate the sample in the trap.

The trap was replaced by several sample loops fabricated from standard, GC grade, 1/8-inch OD stainless-steel tubing. The volume of the lines connecting the trap (or loop) to the GC valves was about 5 mℓ, and constitutes a portion of total loop volume in every case. The loops tested had volumes (total) of 10.7, 18.5, and 32 mℓ. The major effects noted were:

- The peak heights were not significantly greater for the larger loops than for the small.
- The peak areas increased with sample loop volume, but the peaks tended to overlap.

- Increasing carrier flow rate for the larger sample loops helped sharpen the peaks, but did not significantly affect the peak height.

- With proper choice of the Model 950 output filter time constant, about 50 ppb VCM can be detected using the 18.5-mℓ sample loop. (The built-in Model 950 response switch "slow" position was used.)

These general conclusions are supported by the results presented in FIGURES 10 through 13, which are discussed further below.

FIGURE 10 shows the chromatogram obtained with the 10.7-mℓ volume sample loop, using the six-component mixture as before. The Model 950 gain was increased 25-fold to partially make up for the loss of concentration factor provided by the trap, which was 37.4 to 1 in the case of the chromatogram of FIGURE 2. By direct calculation using the simplest assumptions, the peak heights of FIGURE 10 would be expected to be 0.67 as large as those of FIGURE 2. To the extent that the concentration factors for the various peaks are not proportional to trap collection time (sampled volume), this simple calculation will not be valid. The ratios of peak heights for the two chromatograms are given in TABLE 5. Based on the nonlinearity of most of the peak height *vs* sample collection time curves of FIGURE 7, only VCM and 1-butene would be expected to give ratios of about 0.67. While the VCM ratio is lower than expected by about 24%, the 1-butene ratio is higher than expected by about the same percentage.

TABLE 5. RATIO OF PEAK HEIGHTS FOR CHROMATOGRAM OBTAINED USING 10.7-mℓ SAMPLE LOOP (FIGURE 10) TO THOSE OBTAINED FOR A 400-mℓ SAMPLE CONCENTRATED IN THE TRAP (FIGURE 2). WITH KNOWN SENSITIVITY CHANGES, THE RATIO EXPECTED FOR COMPONENTS HAVING A LINEAR RESPONSE WOULD BE 0.67.

Peak No.	Compound	Ratio of Peaks (Figure 10 to Figure 2)
1	Ethylene	3.54
2	Propylene	0.83
3	Vinyl Chloride Monomer	0.53
4	1-butene	0.78
5	Unknown Impurity	0.27
6	1,1- and/or 1,2-dichloroethylene	0.89

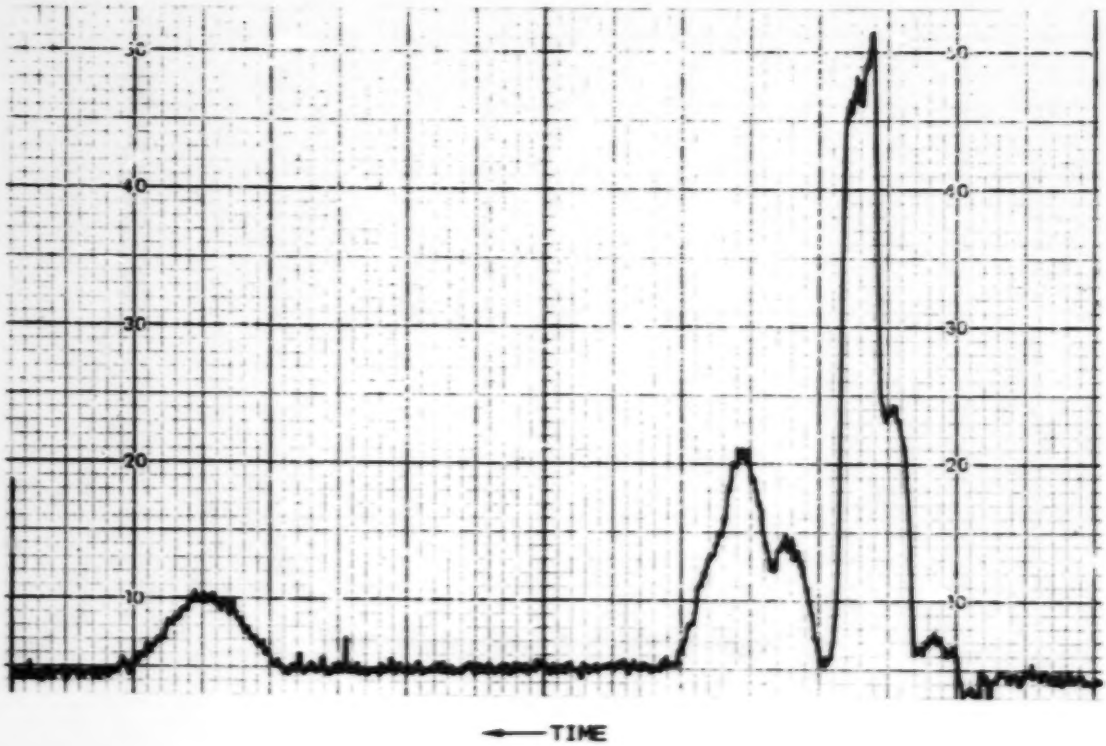
The chromatogram of FIGURE 11 was obtained under the same conditions as that of FIGURE 10, except that the sample loop was increased to 32 mℓ from 10.7 mℓ. The recorder zero was also shifted slightly as a matter of convenience. The important features of this chromatogram are: (a) the peak heights did not increase three-fold compared to that of FIGURE 10; (b) all peaks were broadened by roughly a factor of three; and (c) the peaks overlapped significantly.

THIS CHROMATOGRAM COMPARES DIRECTLY TO THAT OF FIGURE 2 EXCEPT THAT THE MODEL 950 SENSITIVITY WAS INCREASED TWENTY-FIVE TIMES AND THE RECORDER CHART SPEED WAS REDUCED TO ONE-HALF FOR THIS FIGURE. THE CHROMATOGRAM OF FIGURE 2 WAS OBTAINED USING A CONCENTRATION FACTOR OF 37.4. THE PEAK HEIGHTS FOR THIS FIGURE WOULD BE EXPECTED TO BE 67% AS LARGE AS THOSE OF FIGURE 2, BY DIRECT CALCULATION, IF NO OTHER PARAMETERS CHANGED.

OTHER CONDITIONS

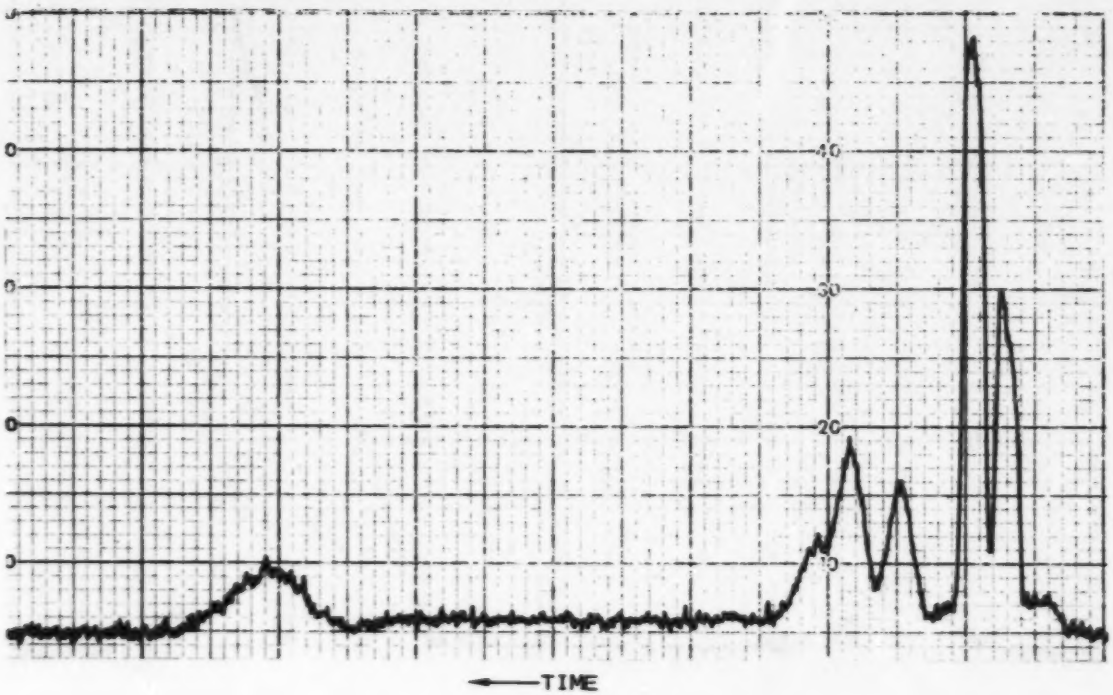
RECORDER:	CHART SPEED ONE-HALF INCH/MIN 100 mV FULL-SCALE SENSITIVITY
MODEL 950 SETTINGS:	1.0 PPM RANGE (2.5 TIMES MORE SENSITIVE THAN FIGURE 2) 10 mV OUTPUT (10 TIMES MORE SENSITIVE THAN FIGURE 2) ZERO AND SPAN POTS AT 7.0 TURNS (AS FOR FIGURE 2) RESPONSE SWITCH IN "FAST" POSITION (AS FOR FIGURE 2)
FLOW RATES:	SAME AS FOR FIGURE 2, EXCEPT 10.7 mℓ SAMPLE LOOP INSTEAD OF TRAP
SAMPLE:	SAME AS FOR FIGURE 2

Figure 10. Chromatogram of Six-Component Mixture in Nitrogen Obtained Using a 10.7 mℓ (Total) Sample Loop in Place of the Trap



THIS CHROMATOGRAM COMPARES DIRECTLY TO THAT OF FIGURE 10, THE LARGER SAMPLE LOOP BEING THE ONLY DIFFERENCE.

Figure 11. Chromatogram of Six-Component Mixture in Nitrogen Obtained Using a 32-ml Sample Loop in Place of the Trap



THIS CHROMATOGRAM COMPARES DIRECTLY TO THAT OF FIGURE 11, WITH ONLY A CHANGE IN CARRIER GAS FLOW RATE.

Figure 12. Chromatogram of Six-Component Mixture in Nitrogen Obtained Using a 32-mℓ Sample Loop in Place of the Trap, and Using 120 mℓ/min of Nitrogen Carrier Gas instead of 75 mℓ/min

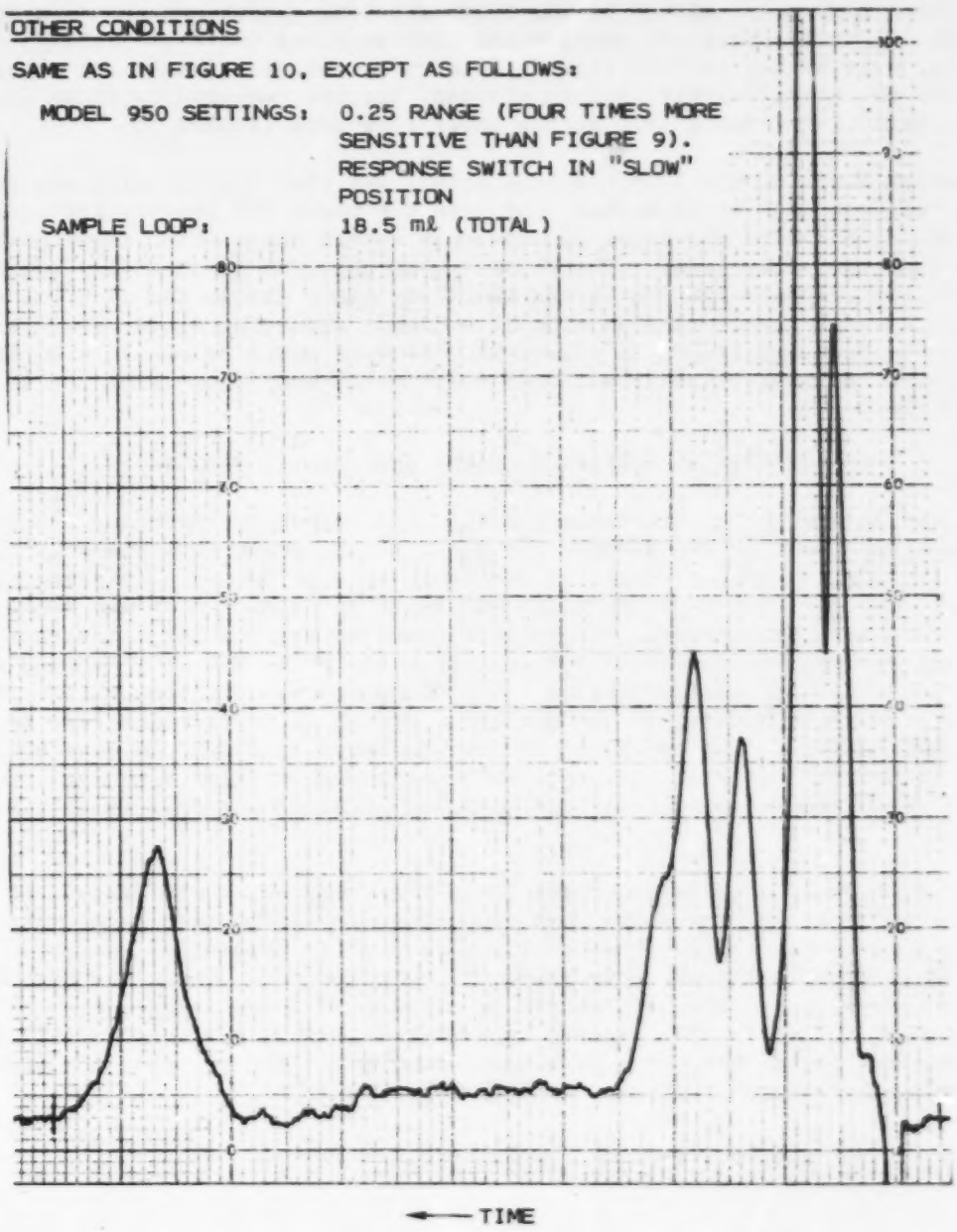

OTHER CONDITIONS
SAME AS IN FIGURE 10, EXCEPT AS FOLLOWS:
MODEL 950 SETTINGS: 0.25 RANGE (FOUR TIMES MORE SENSITIVE THAN FIGURE 9). RESPONSE SWITCH IN "SLOW" POSITION
SAMPLE LOOP: 18.5 mℓ (TOTAL)
TIME

Figure 13. Chromatogram of Six-Component Mixture in Nitrogen Obtained with 18.5 mℓ (Total) Sample Loop in Place of the Trap, and with the Model 950 Sensitivity and Response Speed Changes Indicated

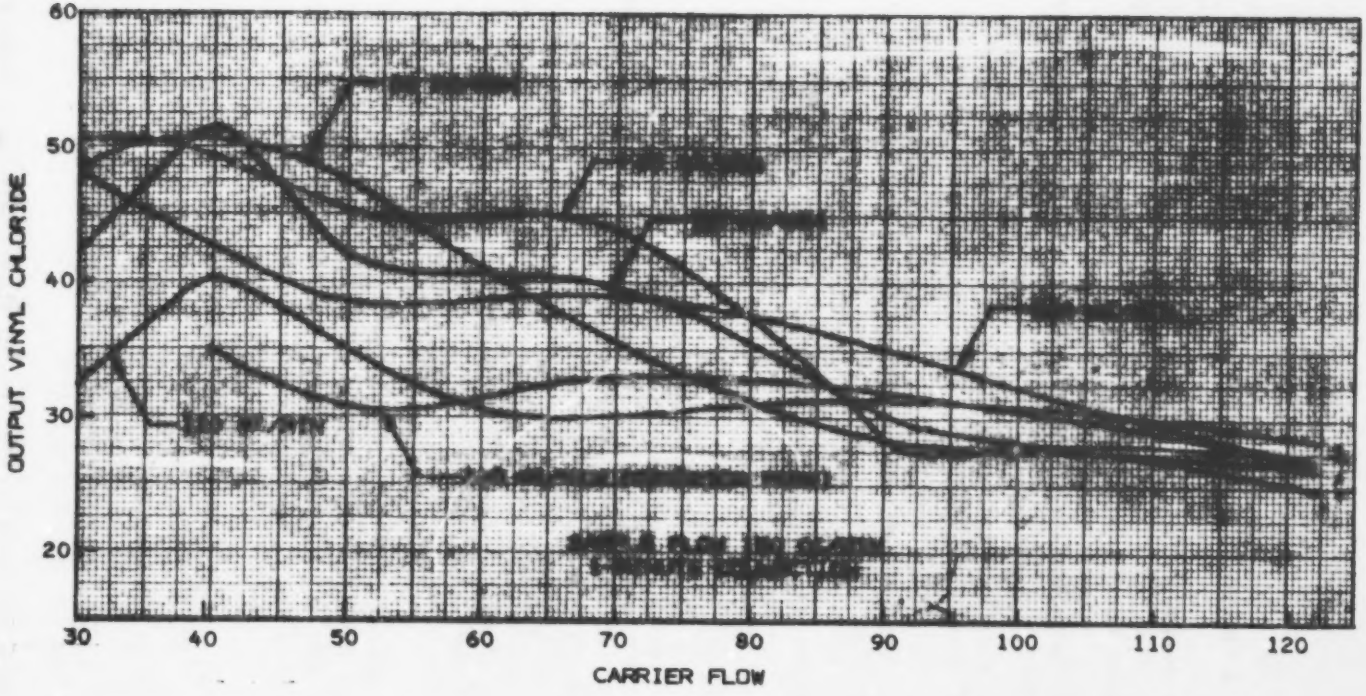
The chromatogram of FIGURE 12 was taken with all conditions the same as for FIGURE 11, except that the carrier gas flow rate was increased from 75 to 120 mℓ/min. The higher carrier flow rate improved the peak resolution markedly, but did not significantly improve the peak heights compared to those obtained with the 10.7-mℓ sample loop at the lower flow rate (FIGURE 10).

An intermediate sample loop (18.5 mℓ total) was then tested, with the carrier flow rate set back to 75 mℓ/min, but with the Model 950 sensitivity increased four-fold, and with the Model 950 response switch set in the "slow" position to reduce the noise level. The chromatogram obtained is shown in FIGURE 13. The "slow" response setting of the Model 950 was a little too slow for optimum peak resolution. (Replacement of a single capacitor would permit optimization.) However, FIGURE 13 illustrates that it would be possible to detect 33 ppb VCM (signal-to-noise ratio of only one to two) when using the 18.5-mℓ sample loop.

4.4 THE EFFECTS OF VARYING OZONATOR AND CARRIER FLOW RATES

As noted in Section 3, Component Testing, the output of the Model 950 chemiluminescence monitor was maximum for equal steady-state flow rates of ozone-rich and VCM containing gases. Those tests were performed by passing the two gas streams directly into the Model 950 reaction chamber. It was believed that roughly equal ozonator and carrier gas flow rates would, therefore, provide the optimum (maximum) VCM peak when the Model 950 was combined with the GC section for system testing. The situation was not that simple, however, presumably because of the nonlinear effect of carrier gas flow rate upon VCM peak heights. The family of curves presented in FIGURE 14 does verify that an optimum ozonator flow rate exists for each carrier flow rate, but the total variation in sensitivity for all data obtained was only about a factor of two.

Several times in the course of the total test program it was discovered that one or more of the flow indicators had become fouled by particulate matter. It is quite possible that part of the data used to obtain the curves of FIGURE 14 were in error due to faulty flow indicators. The minor features of these curves, in particular, should be considered suspect since none of the tests were repeated. The general excellent stability and reproducibility of the monitor throughout the system tests suggests, however, that the basic operational features indicated in FIGURE 14 are valid.



THE CHOICE OF 75 mℓ/MIN CARRIER FLOW RATE AND 100 mℓ/MIN OZONATOR FLOW RATE FOR MOST OF THE TESTS REPORTED WAS BASED UPON THESE CURVES AND UPON THE DESIRE FOR A CONVENIENT ELUTION TIME FOR THE VCM PEAK. THE CHOICE OF 40 mℓ/MIN FOR CARRIER AND 60 mℓ/MIN FOR THE OZONATOR FLOW RATE IS ACTUALLY OPTIMUM WITH REGARD TO SENSITIVITY AND FREEDOM FROM DEPENDENCE UPON MINOR VARIATIONS OF THE TWO FLOW RATES.

Figure 14. The Effect of Varying Carrier Gas Flow Rate upon the Peak Height Observed for 5-ppm VCM in Nitrogen, with Ozonator Flow Rate as a Parameter

5.0 FINAL ACCEPTANCE TEST

The Final Acceptance Test was performed at the EPA facility at Research Triangle Park, North Carolina, with contractor participation. The tests performed may be conveniently divided into three classifications:

- Initial functional checkout, in the same configuration used for the before-delivery test.
- Step-by-step test, modification, and retest to achieve virtual freedom from interference with the VCM peak due to ambient air pollutants.
- Testing in final configuration, which indicated that a 1-ppb VCM detection limit is feasible.

Each of the above classifications of tests is discussed in the following subsections.

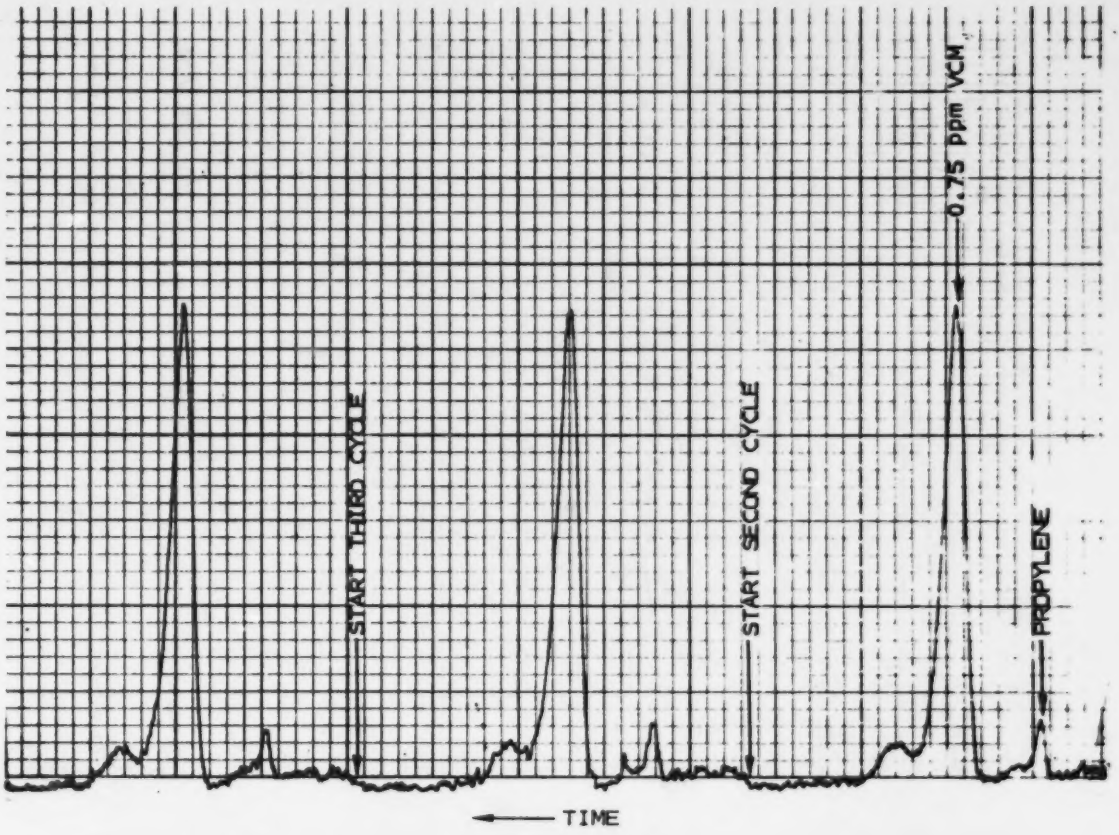
5.1 INITIAL FUNCTIONAL TESTS

FIGURE 15 is a reproduction of a portion of recorder chart showing three successive chromatograms obtained near the end of a four-hour run. All operating conditions are noted on FIGURE 15. These three chromatograms are typical of the reproducibility of the system in all tests. The VCM concentration was approximately 0.75 ppm. A slow zero drift, which is barely noticeable over the time period shown in the figure, occurs whenever the ozonator has been off for a time. The initial zero offset of the chemiluminescence analyzer due to ozone decreases with time for the first day or so of use following a shutdown of a day or more.

Two successive chromatograms obtained with a five-minute (instead of a one-minute) sample collection time are reproduced as FIGURE 16. The only other change made was to reduce the recorder sensitivity five-fold (to 50 mV from 10 mV full scale). The peak heights are slightly smaller in FIGURE 16 than discussed fully in Section 4 of this report.

FIGURE 17 shows chromatogram B, obtained under conditions identical to those of FIGURE 16, and chromatogram A, which was obtained with a tube having a lower (about one-third) VCM permeation rate, but with the recorder gain increased five-fold (to 10 mV from 50 mV full scale. The theoretical rate of VCM peak heights A to B would be 5/3 = 1.67. That observed is within 1% of this value, demonstrating good linearity for 250 and 750 ppb VCM.

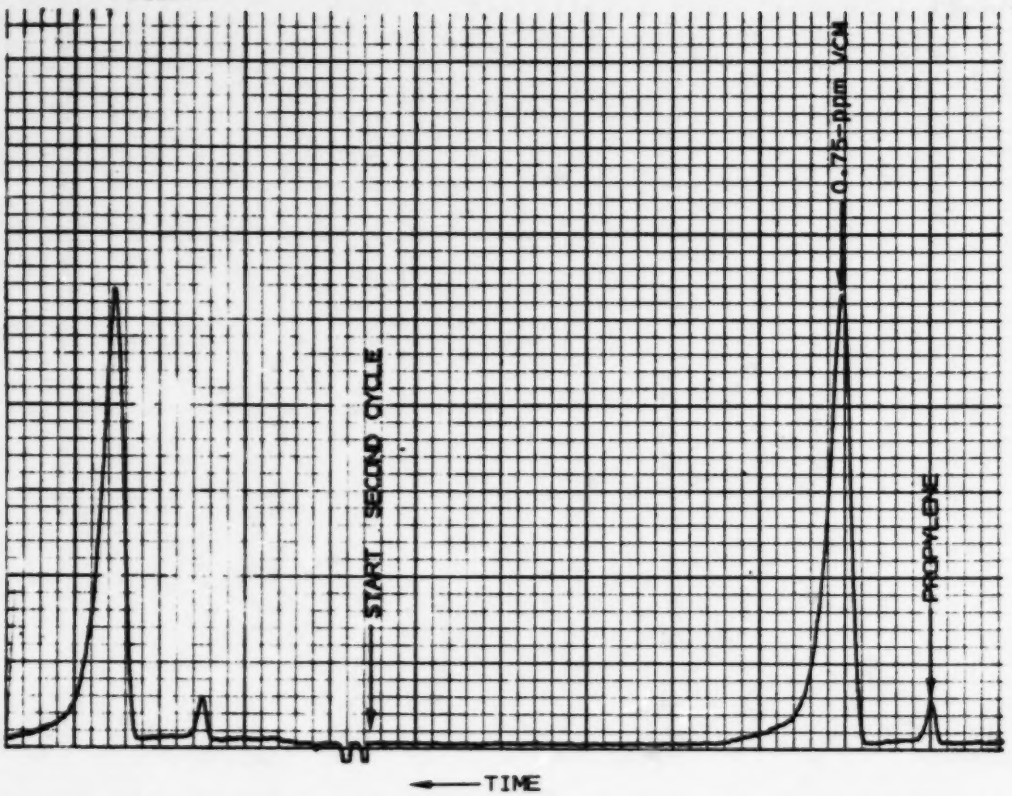
Operation of the monitor on room air samples indicated that there were significant interferences in the 10-ppb VCM range due to unknown atmospheric pollutants. Furthermore, it was found that cigarette smoking in the



OTHER CONDITIONS:

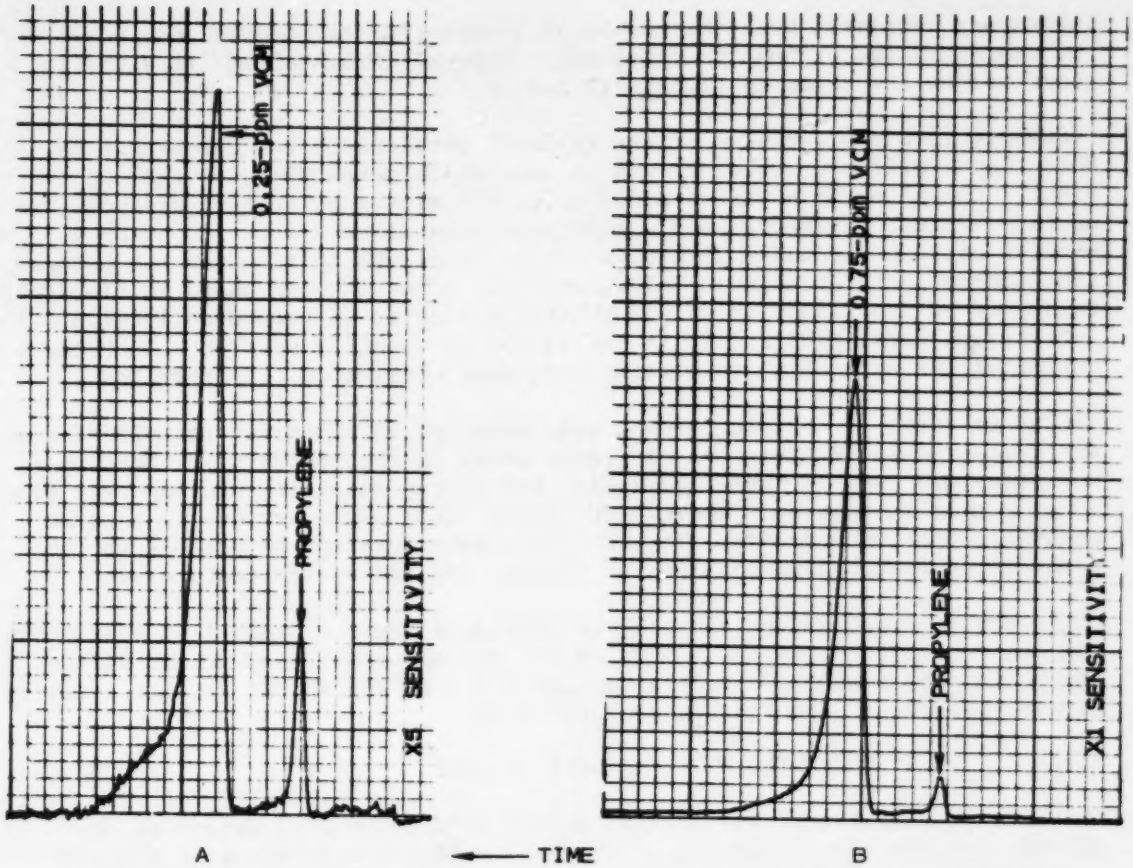
DATE:	DEC 15, 1975
MODEL 6700 TIMING:	(SEE OPERATING INSTRUCTIONS)
	A ON AT 60 S, OFF AT 250 S (GC VALVE A)
	B ON AT 60 S, OFF AT 539 S (GC VALVE B)
	C ON AT 0 S, OFF AT 60 S (SAMPLE COLLECTION)
	D ON AT 60 S, OFF AT 90 S (TRAP HEATING)
	MASTER CYCLE TIMER, 540 S (9-MINUTE CYCLE)
RECORDER:	0 TO 10 mV, 16 INCHES/HOUR
MODEL 950 SETTINGS:	1.0 RANGE
	100 mV OUTPUT
	RESPONSE "FAST"
SAMPLE COLLECTION:	ONE MINUTE AT 150 mℓ/MIN, 0.75 PPM VCM

Figure 15. Three of Many Chromatograms Obtained at EPA Facility using a Permeation Tube Source for 0.75-ppm VCM Concentration



THESE CHROMATOGRAMS WERE OBTAINED WITH OPERATING CONDITIONS IDENTICAL TO THOSE FOR FIGURE 15, EXCEPT THAT THE RECORDER SENSITIVITY WAS REDUCED FIVE-FOLD, THE SAMPLE COLLECTION TIME WAS INCREASED FIVE-FOLD, THE CYCLE TIME WAS 16.7 MINUTES, AND THE MODEL 950 ZERO WAS RESET SLIGHTLY. THE SLIGHT DISCREPANCY IN PEAK HEIGHTS OF FIGURES 15 AND 16 IS DUE TO A FIXED-VOLUME (15 mℓ) SAMPLING ERROR WHICH ARISES FROM EVACUATION OF THE TRAP AND SOME INTERCONNECTING LINES PRIOR TO INITIATION OF SAMPLE COLLECTION. SEE SECTION IV OF THIS REPORT.

Figure 16. Two of Many Chromatograms Obtained at EPA Facility using a Permeation Tube Source for 0.75-ppm VCM Concentration



CHROMATOGRAM B IS IDENTICAL TO THOSE OF FIGURE 16, WHILE CHROMATOGRAM A WAS OBTAINED WITH ONE-THIRD THE LENGTH OF VCM PERMEATION TUBE IN THE LINE, AND WITH THE RECORDER SENSITIVITY INCREASED FIVE-FOLD (TO 10 mV FROM 50 mV FULL SCALE). THE INCREASE IN VCM PEAK HEIGHT IS WITHIN 1% OF THE VALUE CALCULATED, ASSUMING PERFECT LINEARITY. ALSO NOTE THAT THE SMALL PEAK, PROBABLY PROPYLENE, INCREASED FIVE-FOLD. THIS SUGGESTS THAT THE PROPYLENE IMPURITY IS IN THE ONE REMAINING PERMEATION TUBE ONLY.

Figure 17. Chromatogram Showing Linearity of the Monitor Below 1 ppm VCM

laboratory increased both the number of interfering substances and, possibly, the concentration of some interferants. Typical chromatograms illustrating these points are shown in FIGURES 18 and 19.

FIGURE 18 is a reproduction of the relevant portions of two chromatograms. Note that a different recorder was in use, which makes time increase to the right. Chromatogram A was obtained using a 5-minute collection of room air at 150 mℓ/min. Chromatogram B was obtained immediately after A, using 4.25 minutes of room air and 0.75 minute of 0.25-ppm VCM in air from the permeation source, both at a 150-mℓ/min flow rate. The VCM peak shown in FIGURE 18B is due to an equivalent of 38 ppb VCM for 5 minutes of sample collection. The interfering peak, FIGURE 18A, is equivalent to about 12 ppb VCM. Both these chromatograms were obtained with no cigarette smoking in the laboratory.

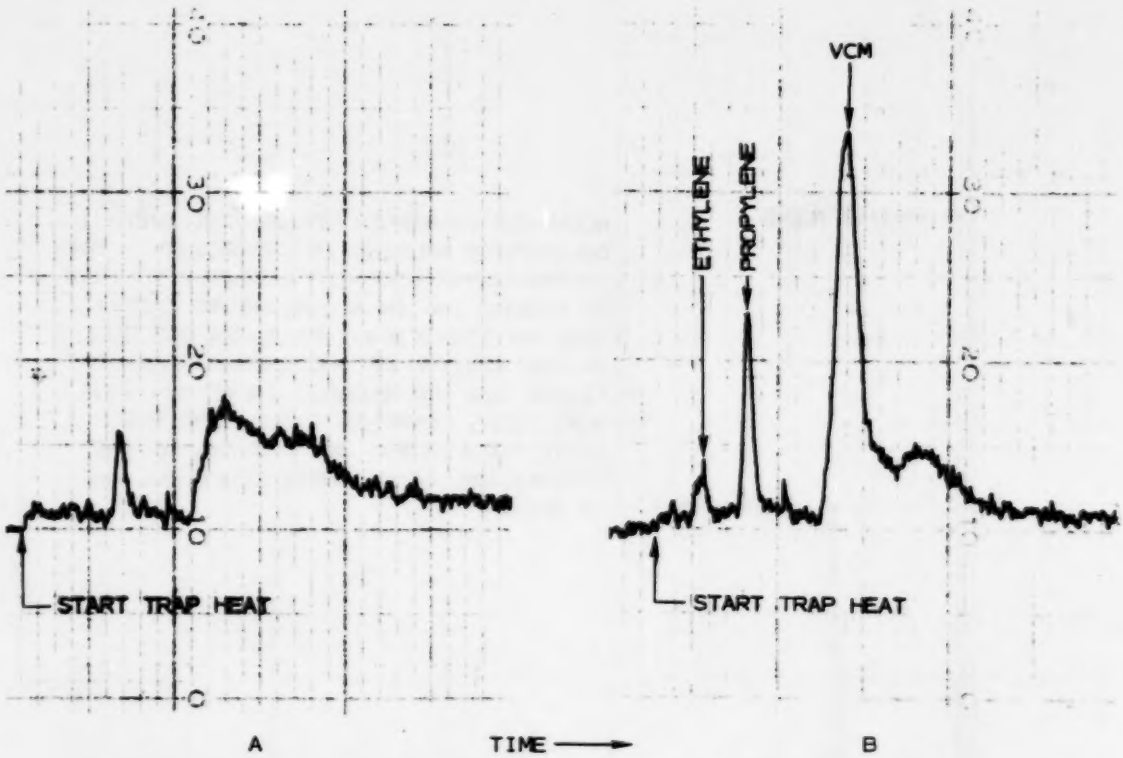
FIGURE 19 shows a complete chromatogram obtained on a 5-minute sample of room air collected while there was cigarette smoke in the laboratory. Note that the propylene peak increases markedly, and that a substance eluting very soon after VCM is in cigarette smoke. The three later peaks are due to unknown cigarette smoke components. The last two peaks were not detectable in the room air; corresponding portions of FIGURES 18A and B were featureless.

While the original intent had been to provide a monitor capable of monitoring VCM and two related compounds such as the dichloroethylenes, it was decided that elimination of the direct interferences with VCM should receive priority for the balance of the Final Acceptance Test

5.2 TESTS CONDUCTED WITH CARBOWAX COLUMNS

The GC oven temperature was increased from 90°C to 98°C to determine the effect upon the air pollutants which were found to interfere with the VCM peak. No significant improvement over the data of FIGURE 19 was obtained. The Beckman analysis column was then replaced with a column previously evaluated by the EPA. This analysis column was 1 m long and consisted of 3-mm ID Teflon tubing packed with 0.4% Carbowax 1500 (or Carbopack A, Supelco, Inc.) The Beckman stripper column was left in place. This configuration was employed for the balance of the Final Acceptance Test. The only parameters subsequently varied to eliminate interference were the GC oven temperature and the time after initiation of trap heating at which back flush of the stripper was initiated.

Tests of the new column configuration were conducted at about 30, 54, and 70°C for the GC oven temperature. It was found that at 70°C and with back flush of the stripper column initiated at 120 to 130 seconds after start of trap heating (equivalent to normal GC sample injection time), the troublesome interferences were eliminated. This is illustrated by chromatograms A and B of FIGURE 20. In retrospect, it is possible that the back flush was being initiated too soon, which would cause a loss of part of the VCM peak as well as the immediately following interferants. The test record does not clearly indicate that the time could be reduced further without reducing the VCM peak.



ROOM AIR (5-MINUTE COLLECTION) CHROMATOGRAM (A) AND ROOM AIR (4.25 MIN) PLUS ABOUT 45 SECONDS COLLECTION OF 0.25 PPM OF VCM FROM PERMEATION TUBE SOURCE (B). THESE CHROMATOGRAMS CLEARLY INDICATE THE PRESENCE OF ONE OR MORE SUBSTANCES IN THE ROOM AIR WHICH WOULD INTERFERE WITH VCM AT A LEVEL OF A FEW PPB. THE RECORDER SENSITIVITY WAS ROUGHLY 2 PPB VCM PER DIVISION FOR A 0.75-LITER SAMPLE (5-MINUTE COLLECTION AT FLOW RATE OF 150 mℓ/MIN).

Figure 18. Chromatograms Indicating Presence of Interfering Pollutants

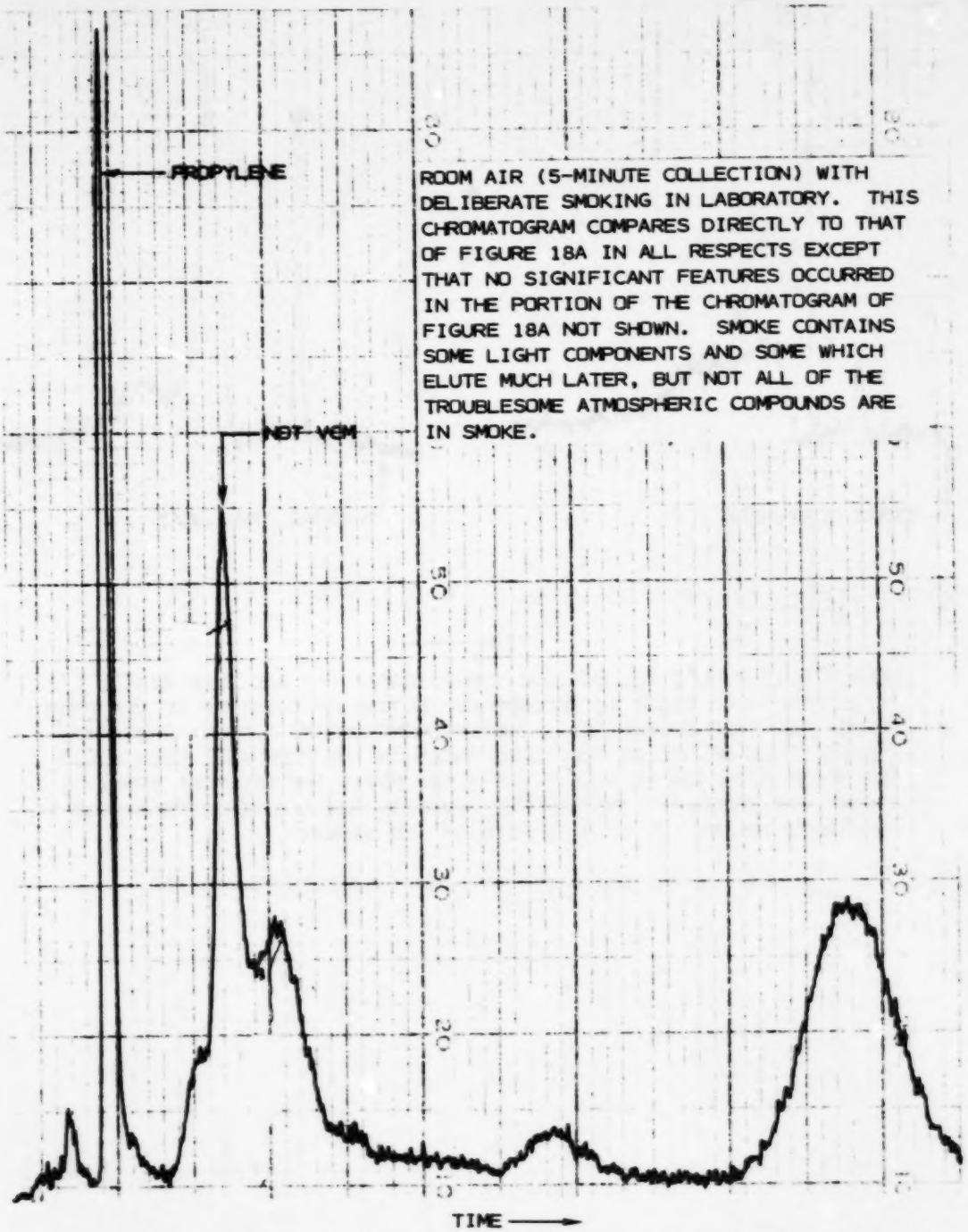
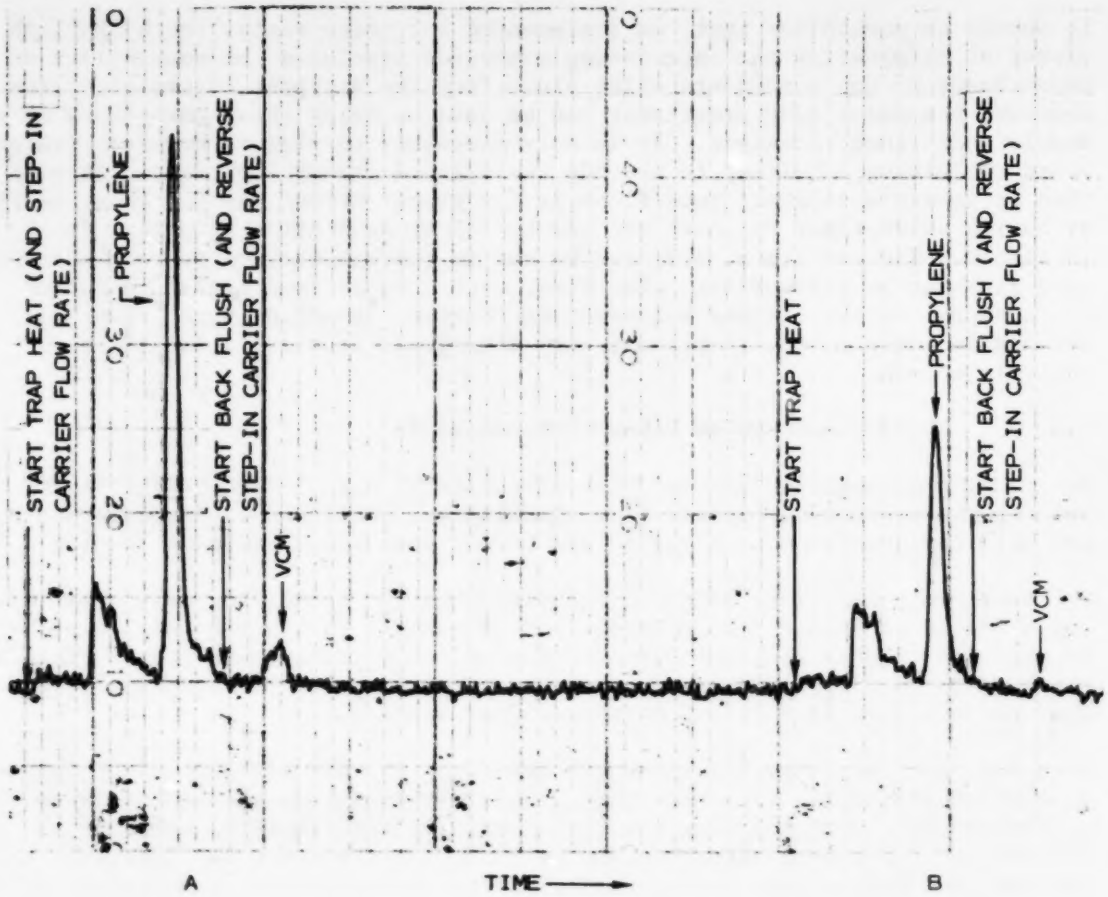

PROPYLENE
NBT VEM
ROOM AIR (5-MINUTE COLLECTION) WITH DELIBERATE SMOKING IN LABORATORY. THIS CHROMATOGRAM COMPARES DIRECTLY TO THAT OF FIGURE 18A IN ALL RESPECTS EXCEPT THAT NO SIGNIFICANT FEATURES OCCURRED IN THE PORTION OF THE CHROMATOGRAM OF FIGURE 18A NOT SHOWN. SMOKE CONTAINS SOME LIGHT COMPONENTS AND SOME WHICH ELUTE MUCH LATER, BUT NOT ALL OF THE TROUBLESOME ATMOSPHERIC COMPOUNDS ARE IN SMOKE.
TIME

Figure 19. Chromatogram Indicating the Presence of Interfering Compounds in Cigarette Smoke



CHROMATOGRAM A WAS FOR 10 SECONDS OF 0.25-PPM VCM IN CLEAN AIR WITH BALANCE OF FIVE MINUTES COLLECTION OF ROOM AIR. CHROMATOGRAM B WAS FOR ROOM AIR ONLY. SMOKING WAS NOT CONTROLLED DURING THESE TESTS, WHICH ACCOUNTS FOR THE MAJOR VARIATION IN THE PROPYLENE PEAKS. NOTE THAT THERE IS LESS THAN ONE CHART DIVISION PEAK (PROBABLY NOISE) AT THE VCM ELUTION TIME FOR CHROMATOGRAM B. THE INTERFERENCE IS, THEREFORE, LESS THAN 2 PPB VCM EQUIVALENT, AND PROBABLY LESS THAN 0.5 PPB.

Figure 20. Two Chromatograms Obtained after Modifying Operating Conditions to Eliminate Interference of Cigarette Smoke and of Unknown Atmospheric Pollutants with VCM Determination

It should be emphasized that, as implemented for these tests, the back-flush method of eliminating the interfering compounds precluded the possibility of measurement of any components which elute from the stripper column after VCM. However, the Model 6700 programmer can be used to delay these components by a double back-flush technique. It is only necessary to plug in an extra timing board (no wiring required) to provide two valve-A driver functions. It will then be possible to start back flush at the proper moment (as for these tests) by having valve timer A-1 turn off 120 to 130 seconds after trap heat is initiated. The new timer, A-2, can be set to operate valve-A to resume forward flush at an appropriate later time, until the desired peaks are out of the stripper column. Timer A-2 may then initiate permanent back flush, as A-1 did in these tests, to prevent very slow peaks from ever reaching the analysis column.

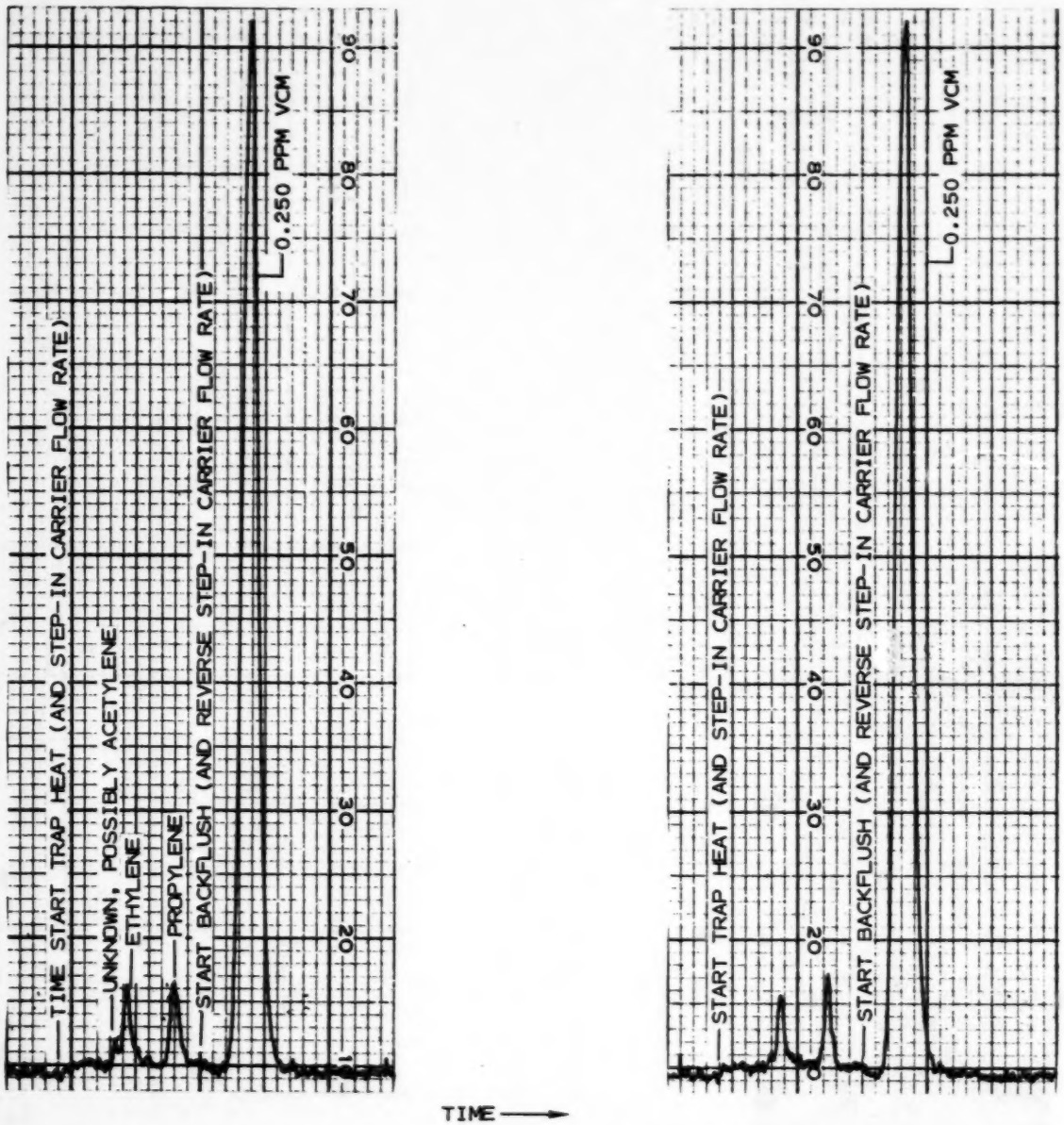
5.3 TESTS PERFORMED IN FINAL CONFIGURATION

The final configuration provided for virtually no interference with the VCM peak in the prevailing ambient air. Smoking was permitted in the laboratory, and only the propylene peak varied due to the variations in smoke loading.

The operating conditions of the permeation tube VCM calibrator were verified and a series of stable chromatograms was obtained. The two successive chromatograms of FIGURE 21 are typical of the noise level and peak reproducibility obtained for 0.25-ppm VCM in precleaned air collected in the trap for five minutes at a flow rate of 150 mℓ/min (750-mℓ sample).

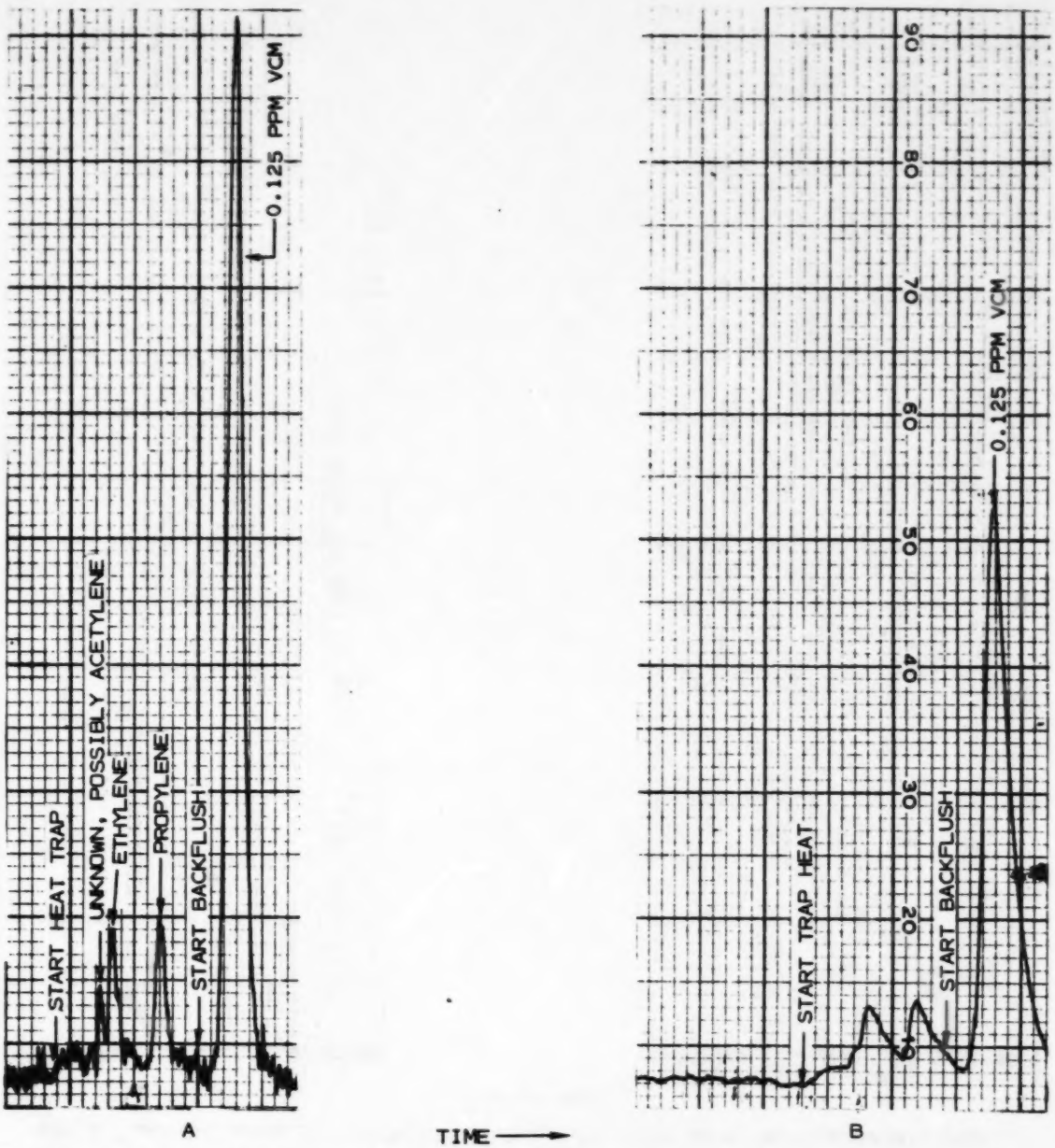
A second test result is indicated by comparison of the base-line noise levels in FIGURES 20 and 21. The Model 950 sensitivity was increased ten-fold, with a corresponding decrease in recorder sensitivity for FIGURE 21 compared to FIGURE 20. The approximate equality of noise for the two cases indicates that the dominant noise comes from the PMT. It is very probable that variations in ozone concentration are the major cause of low frequency noise. The ozonator lamp current varies with line voltage. This causes variations in the ozone concentration, which affects both the base-line and the VCM peak heights.

The permeation tube calibrator parameters were then adjusted to provide a sample of 0.125-ppm VCM in air. The chromatogram of FIGURE 22A is typical of several obtained. Note that the Model 950 gain was increased about a factor of two to provide almost full-scale peaks for 0.125-ppm VCM, and that the noise increased proportionately in FIGURE 22A compared to that of FIGURE 21, as would be expected. FIGURE 22B is a reproduction of a chromatogram obtained with all conditions the same as for FIGURE 22A except that the Model 950 response switch was placed in the "slow" position. The distortion and attenuation of the peaks indicate that the "slow" time constant is four to five times too large for optimum performance in this application. This situation could be corrected by changing only one capacitor in the Model 950 preamplifier board.


TIME START TRAP HEAT (AND STEP-IN CARRIER FLOW RATE)
UNKNOWN, POSSIBLY ACETYLENE
ETHYLENE
PROPYLENE
START BACKFLUSH (AND REVERSE STEP-IN CARRIER FLOW RATE)
0.250 PPM VCM
START TRAP HEAT (AND STEP-IN CARRIER FLOW RATE)
START BACKFLUSH (AND REVERSE STEP-IN CARRIER FLOW RATE)
0.250 PPM VCM
TIME

THESE CHROMATOGRAMS ALSO SHOW THAT THE MAJOR NOISE IS FROM THE PMT, SINCE THE MODEL 950 SENSITIVITY IS UP TEN-FOLD AND RECORDER SENSITIVITY IS DOWN TEN-FOLD COMPARED TO FIGURE 20

Figure 21. Relevant Portions of Two Consecutive Chromatograms Obtained Using 0.25-ppm VCM in Clean Air from Permeation Tube, Collected for Five Minutes at 150-mℓ/minute



THE MODEL 950 RESPONSE SWITCH WAS SET "FAST" FOR A AND "SLOW" FOR B. THE SLOW TIME CONSTANT SHOULD BE REDUCED BY A FACTOR OF ABOUT FOUR FOR OPTIMUM FILTERING IN THIS APPLICATION

Figure 22. Two Successive Chromatograms Obtained for Five-Minute Collections of 0.125-ppm VCM in Nitrogen from Permeation Tube Source at Flow Rate of 150 mℓ/minute

The low frequency variations in baseline still seen in FIGURE 22B would then be no more than about five times as large, or about ±1% of recorder scale maximum. This would result in a detectable limit of about 1.5-ppb VCM for a single measurement (signal-to-noise ratio of about one). Comparison of several chromatograms to visually screen out the random noise effect would, of course, permit a still lower detectable limit. Furthermore, by increasing either the sample flow rate or the collection time, the VCM concentration factor could be doubled (provided the trap temperature during sample collection was less than about 35°C) to make it possible to detect less than 1 ppb VCM with a single observation.